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PB-292 460

Radionuclide Interactions with Soil and Rock Media Volume 1: Processes Influencing Radionuclide Mobility and Retention, Element Chemistry and Geochemistry, Conclusions and Evaluation

Battelle Pacific Northwest Labs, Richland, WA

Prepared for

Office of Radiation Programs, Las Vegas, NV

Aug 78

United States
Environmental Protection
Agency

Office of Radiation Programs
Las Vegas Facility
P.O. Box 15027
Las Vegas NV 89114

EPA 520/6-78-007-A
August 1978

PB 292460

Radiation

EPA

Radionuclide Interactions with Soil and Rock Media

Volume 1:
Processes Influencing Radionuclide Mobility and Retention

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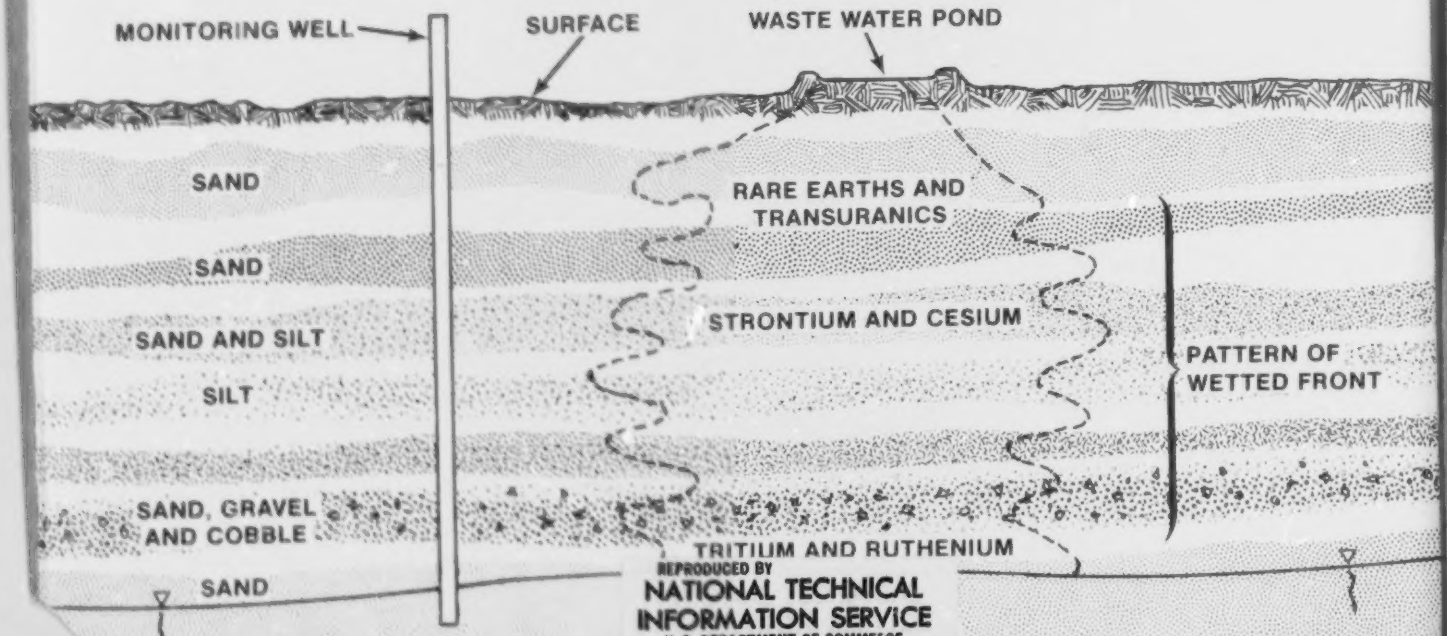
Conclusions and Evaluation


MONITORING WELL
SURFACE
WASTE WATER POND
SAND
RARE EARTHS AND TRANSURANICS
SAND
STRONTIUM AND CESIUM
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TECHNICAL REPORT DATA
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1. REPORT NO. EPA 520/6-78-007-a	2.	3. RECIPIENT'S ACCESSION NO. PB292460
4. TITLE AND SUBTITLE Radionuclide Interactions with Rock and Soil Media Volume I (text)		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Lloyd L. Ames and Dhanpat Rai		8. PERFORMING ORGANIZATION REPORT NO. N/A
9. PERFORMING ORGANIZATION NAME AND ADDRESS Battelle Pacific Northwest Laboratories Richland, WA 99352		10. PROGRAM ELEMENT NO. N/A
		11. CONTRACT/GRANT NO. (Contract) 68-03-2514
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Radiation Programs-Las Vegas Facility P.O. Box 15027 Las Vegas, NV 89114		13. TYPE OF REPORT AND PERIOD COVERED Final
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES Vol.I Narrative discussion of 1) Processes influencing radionuclide mobility and retention, 2) Element chemistry and geochemistry, 3) Conclusions and evaluation. Vol.II Annotated bibliography (Pt. A: Citations A-Mc; Pt. B: M-Z)

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Radioactive Isotopes	Chemical Removal	Geologic Disposal	0802
Radioactive Wastes	Reaction Kinetics	Radioactive Waste	0705
Radiochemistry	Chemical Reactivity	Disposal	0702
Soil Properties	Chemical Reactions	Radioactive Waste -	1807
Soils	Geology	Media Interaction	1808
			0807

18. DISTRIBUTION STATEMENT Release unlimited; available on request, subject to supply, at address shown in block 12.	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 330
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE PC A15/MF A01

EPA 520/6-78-007-a
August 1978
Volume 1 of 2

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Volume 1: Processes Influencing Radionuclide Mobility and Retention
Element Chemistry and Geochemistry
Conclusions and Evaluation

by
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Final Report for Contract 68-03-2514

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PREFACE

The Office of Radiation Programs carries out a national program designed to evaluate the exposure of man to ionizing and nonionizing radiation, and to promote the development of controls necessary to protect the public health and safety and assure environmental quality. A current area of great interest and effort within the EPA is the development of environmental protection criteria and standards for the management of radioactive wastes. Accidental or deliberate interactions of such wastes with various geologic media dictate that the Agency have access to current knowledge concerning the occurrence and mobility of selected radionuclides in the lithosphere. Herein lies the purpose and scope of the present study.

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W. D. Rowe, Ph.D.
Deputy Assistant Administrator
for Radiation Programs

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ACKNOWLEDGMENTS

The authors would like to acknowledge the following persons who participated in the review of this report:

Mr. H. J. Horton,
Savannah River Laboratory

Mr. W. K. Summers,
Consulting Hydrogeologist
Socorro, New Mexico

Dr. D. Isherwood,
Lawrence Livermore Laboratories

Mr. G. Grisak,
Hydrology Research Division
Environment Canada

Mr. G. L. Meyer,
Office of Radiation Programs
U.S. Environmental Protection Agency

Dr. D. C. Hoffman,
Chemical and Nuclear Chemistry Division
Los Alamos Scientific Laboratory

Mr. J. P. Hamric,
Director, Nuclear Fuel Cycle Division
DOE Idaho Operations Office

Funding was provided by the EPA Office of Research and Development and the Office of Energy, Minerals and Industry.

The authors also wish to thank the following Battelle staff members who assisted in the report preparation: S. I. Thoreson, D. J. Kennedy, M. V. Heid, and S. R. Gano.

SECTION 1

INTRODUCTION

The nuclear industry, like many other industries, produces wastes. Part of these wastes are radioactive and biologically hazardous without management. In general, the hazard represented by the radioactive wastes decreases with isolation and storage, due to radioactive decay with passing time. However, some of these wastes contain radioisotopes of americium, curium, iodine, neptunium, plutonium, technetium and uranium with half-lives of many thousands of years, so that these isotopes will persist.

Selected radioactive wastes have been, and are being, disposed by land burial. Barriers around storage and disposal sites are generally constructed to safeguard against radioactive contamination of the environment by wind erosion or by trespassing of unauthorized personnel. However, in the case of accidental spills or breach of barriers, the radioactive elements can enter the surrounding environment. Water is one of the main transporting agents in terrestrial environments and will control dissemination of the radionuclides below the ground surface. The biological retention and mobility of the radionuclides in geologic regimes will be governed by the physical and chemical characteristics of the geohydrologic system. The composition of the water in the geohydrologic system is determined by the adsorption-desorption and precipitation-dissolution reactions between the water and the solid phases making up the soils, sediments and rocks. As one of the principal controls of the concentration of radionuclides in the geohydrologic system at a given time, the interactions of the radionuclides with soils and rocks in an aqueous system become of primary interest to understanding radionuclide migration and retention. As a consequence, the present work was undertaken to critically review the literature available through 1976 concerned with radionuclide interactions with soils and rocks. The objectives of this study were to:

1. summarize and critically review the available information on radionuclide interactions with the geologic media, and
2. determine the deficiencies in the available data and outline future work required to correct these deficiencies.

Several reviews already are available that include radionuclide interactions with geologic materials (Gera, 1975; Borg et al., 1976a; Dames and Moore, 1976; Routson, 1973; Bensen, 1960). However, these reviews do not cover but a limited number of elements, refer to work done only in specific geographical areas or their emphasis is not primarily the interactions between geologic media and radionuclides.

METHODS AND CONSTRAINTS

The fission and activation products that are present in nuclear processing and other radioactive wastes and are most biologically hazardous were selected for study. For each selected element, pertinent available literature on natural distribution in soils and rocks, thermodynamic data for solid and solution species, chemistry of the element, radionuclide adsorption-desorption, radionuclide precipitation and dissolution and the mobility of the element in laboratory and field situations was collected. These data were organized and used to critically review the present state of knowledge of the interactions of radionuclides with geologic media.

Due to time (14 months) and level of effort (one man year) constraints, the present study was limited in scope. Soil and rock reactions with a selected group of radionuclides were thoroughly reviewed. Less effort was spent on elemental chemistry and natural distribution. Available thermodynamic data for various solids and solution species used in this study were not critically evaluated by the present writers. However, the thermodynamic data were checked for internal consistency. Laboratory work, field work and modeling were excluded from the study.

Selection of Radionuclides

Based upon radionuclide concentrations in radioactive wastes (Table 1-1), 19 potentially biologically hazardous elements were chosen for critical review including americium, antimony, cerium, cesium, cobalt, curium, europium, iodine,

TABLE 1-1. LWR PLANT WASTE FROM URANIUM FUELS REPROCESSING* (SCHNEIDER AND PLATT, 1974)

SELECTED ACTINIDES, curies/metric ton of U

Radionuclide	Separation	1 Year	10 Years	100 Years	1,000 Years	10,000 Years
^{225}Ra	3.48×10^{-8}	3.50×10^{-8}	4.22×10^{-8}	7.31×10^{-7}	6.94×10^{-5}	5.54×10^{-3}
^{226}Ra	1.97×10^{-8}	2.85×10^{-8}	1.09×10^{-7}	1.11×10^{-6}	7.22×10^{-5}	2.91×10^{-3}
^{229}Th	3.49×10^{-8}	3.50×10^{-8}	4.22×10^{-8}	7.31×10^{-7}	6.94×10^{-5}	5.54×10^{-3}
^{230}Th	2.04×10^{-5}	2.05×10^{-5}	2.09×10^{-5}	3.42×10^{-5}	3.86×10^{-4}	3.74×10^{-3}
^{233}U	2.31×10^{-7}	1.84×10^{-6}	1.49×10^{-5}	1.47×10^{-4}	1.52×10^{-3}	1.56×10^{-2}
^{234}U	3.77×10^{-3}	3.95×10^{-3}	6.64×10^{-3}	2.56×10^{-2}	4.56×10^{-2}	4.45×10^{-2}
^{237}Np	3.40×10^{-1}	3.40×10^{-1}	3.41×10^{-1}	3.45×10^{-1}	3.67×10^{-1}	3.74×10^{-1}
^{239}Np	1.76×10^{1}	1.76×10^{1}	1.75×10^{1}	1.74×10^{1}	1.60×10^{1}	7.10×10^{0}
^{239}Pu	1.62×10^{0}	1.62×10^{0}	1.62×10^{0}	1.67×10^{0}	2.05×10^{0}	4.02×10^{0}
^{240}Pu	2.37×10^{0}	2.63×10^{0}	4.52×10^{0}	8.90×10^{0}	8.25×10^{0}	3.28×10^{0}
^{241}Am	1.52×10^{2}	1.52×10^{2}	1.55×10^{2}	1.44×10^{2}	3.43×10^{1}	1.31×10^{-1}
^{243}Am	1.76×10^{1}	1.76×10^{1}	1.75×10^{1}	1.74×10^{1}	1.60×10^{1}	7.10×10^{0}
^{242}Cm	1.93×10^{4}	4.08×10^{3}	3.16×10^{0}	2.09×10^{0}	3.46×10^{-2}	5.24×10^{-20}
^{245}Cm	2.76×10^{-1}	2.76×10^{-1}	2.76×10^{-1}	2.74×10^{-1}	2.56×10^{-1}	1.31×10^{-1}

SELECTED FISSION PRODUCTS, curies/metric ton of U

Radionuclide	Separation	1 Year	10 Years	100 Years	1,000 Years	10,000 Years
^{3}H	6.92×10^{2}	6.54×10^{2}	3.94×10^{2}	2.47×10^{0}	2.35×10^{-22}	0.00
^{79}Se	3.98×10^{-1}	3.98×10^{-1}	3.98×10^{-1}	3.98×10^{-1}	3.94×10^{-1}	1.37×10^{-1}
^{89}Sr	9.72×10^{4}	7.48×10^{2}	7.05×10^{-17}	0.00	0.00	0.00
^{90}Sr	7.68×10^{4}	7.50×10^{4}	6.01×10^{4}	6.53×10^{3}	1.50×10^{-6}	0.00
^{93}Zr	1.46×10^{0}	1.46×10^{0}	1.46×10^{0}	1.46×10^{0}	1.46×10^{0}	1.45×10^{0}
^{95}Zr	2.77×10^{5}	5.65×10^{3}	3.40×10^{-12}	0.00	0.00	0.00
^{99}Tc	1.43×10^{1}	1.43×10^{1}	1.43×10^{1}	1.43×10^{1}	1.43×10^{1}	1.39×10^{1}
^{103}Ru	8.83×10^{4}	1.48×10^{2}	1.54×10^{-23}	0.00	0.00	0.00
^{106}Ru	4.10×10^{5}	2.06×10^{5}	4.15×10^{2}	4.58×10^{-25}	0.00	0.00
^{107}Pd	1.10×10^{-1}	1.10×10^{-1}	1.10×10^{-1}	1.10×10^{-1}	1.10×10^{-1}	1.10×10^{-1}
^{124}Sb	8.53×10^{1}	1.26×10^{0}	4.08×10^{-17}	0.00	0.00	0.00
^{125}Sb	7.99×10^{3}	6.18×10^{3}	6.14×10^{2}	5.70×10^{-8}	0.00	0.00
^{126}Sn	5.46×10^{-1}	5.46×10^{-1}	5.46×10^{-1}	5.46×10^{-1}	5.42×10^{-1}	5.10×10^{-1}
^{129}I	3.74×10^{-2}	3.75×10^{-2}	3.75×10^{-2}	3.75×10^{-2}	3.75×10^{-2}	3.74×10^{-2}
^{134}Cs	2.15×10^{5}	1.53×10^{5}	7.30×10^{3}	4.47×10^{-10}	0.00	0.00
^{135}Cs	4.96×10^{-1}	4.96×10^{-1}	4.96×10^{-1}	4.96×10^{-1}	4.95×10^{-1}	4.94×10^{-1}
^{137}Cs	1.07×10^{5}	1.04×10^{5}	8.48×10^{4}	1.06×10^{4}	9.92×10^{-6}	0.00
^{141}Ce	5.64×10^{4}	2.29×10^{1}	0.00	0.00	0.00	0.00
^{144}Ce	7.71×10^{5}	3.16×10^{5}	1.04×10^{2}	0.00	0.00	0.00
^{147}Pm	9.80×10^{4}	7.52×10^{4}	6.96×10^{3}	3.19×10^{-7}	0.00	0.00
^{148}Pm	3.19×10^{1}	7.71×10^{-2}	2.15×10^{-25}	0.00	0.00	0.00
^{151}Sm	1.47×10^{3}	1.46×10^{3}	1.36×10^{3}	6.46×10^{2}	5.12×10^{-1}	0.00
^{152}Eu	1.14×10^{1}	1.07×10^{1}	6.38×10^{0}	3.53×10^{-2}	9.45×10^{-25}	0.00
^{154}Eu	6.76×10^{3}	6.47×10^{3}	4.38×10^{3}	8.89×10^{1}	1.05×10^{-15}	0.00
^{155}Eu	9.84×10^{3}	6.71×10^{3}	2.14×10^{2}	2.32×10^{-13}	0.00	0.00

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*Assumptions: power 30 megawatts/metric ton, exposure 33,000 megawatt-days/metric ton, 3.3% enriched U, flux 2.92×10^{13} N/cm^2-sec, spent fuel reprocessed 150 days after discharge, 0.5% fuel loss to waste.

neptunium, plutonium, promethium, radium, ruthenium, strontium, technetium, thorium, tritium, uranium and zirconium. This list includes most of the elements that are of both immediate and long-term concern. Cobalt is not listed in Table 1-1 because it is not an actinide or a fission product. It is included here because as ^{60}Co it is widely used in gamma irradiation sources and occurs in other cobalt-containing materials that have been exposed to a neutron flux. Cobalt can often be found in industrial and medical radioactive wastes. Radium, a uranium and thorium decay chain product, is listed with the parent actinides for convenience in Table 1-1. The selected radionuclides, for example, also include the fission products and actinides calculated to be the most radiotoxic in the leachate from German high level waste-borosilicate glasses (Scheffler et al., 1977).

Collection of Pertinent Literature

Because of limited time and resources available for the literature collection and abstracting, an attempt was made to use already available bibliographical data to critically review radionuclide interactions with geological media. However, it soon became apparent that the available bibliographies were not adequate (Environmental Plutonium Data Base Group, 1972, 1973; Martin et al., 1974; Faust et al., 1975; Francis et al., 1975; Ames et al., 1976) because

1. they did not deal with all the 19 elements of interest,
2. their main emphasis was other than radionuclide reactions with geologic media,
3. the information regarding elements was often widely scattered through the bibliography, or
4. they did not include all aspects pertinent to radionuclide interactions with geologic media.

It was necessary to compile a comprehensive bibliography dealing with all aspects of pertinence for the present study. The resulting annotated bibliography, prepared by the senior author, is published as Volume 2 of this study. The bibliography was then utilized to summarize and critically evaluate the interactions of the 19 elements with soils and rocks.

As used in the following sections, a soil is defined as consisting of disintegrated rock and sometimes organic material with associated flora and fauna. The term soil is used in an engineering sense, and is not tied to any specific depth such as the root zone. A sediment has a different origin than a soil, but is considered here to be composed of essentially the same materials. A rock is a consolidated material composed of several mineral phases and may also contain organic matter.

REFERENCES

Ames, L. L., Dhanpat Rai and R. J. Serne. 1976. A Review of Actinide-Sediment Reactions with an Annotated Bibliography. BNWL-1983.

Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Borg, I. Y., R. Stone, H. B. Levy and L. D. Ramspott. 1976a. Information Pertinent to the Migration of Radionuclides in Ground Water at the Nevada Test Site. Part 1: Review and Analysis of Existing Information. UCRL-52078, Pt. 1.

Borg, I. Y., R. Stone, H. B. Levy and L. D. Ramspott. 1976b. Information Pertinent to the Migration of Radionuclides in Ground Water at the Nevada Test Site. Part 2: Annotated Bibliography. UCRL-52078, Pt. 2.

Dames and Moore. 1976. Development of Monitoring Programs for ERDA Owned Radioactive Low-Level Waste Burial Sites.

Environmental Plutonium Data Base Group. 1972. Environmental Aspects of Plutonium. A Selected, Annotated Bibliography. ORNL-EIS-72-21.

Environmental Plutonium Data Base Group. 1973. Environmental Aspects of Plutonium and Other Elements. A Selected, Annotated Bibliography. ORNL-EIS-73-21 (Suppl. 1).

Faust, R. A., F. M. Martin, C. T. Sanders, and S. S. Talmage (comps. and eds.). 1975. Environmental Aspects of the Transuranics: A Selected, Annotated Bibliography. ORNL-EIS-75-21-5.

Francis, C. W., S. S. Talmage and B. B. McMullin. 1975. Radionuclide Movement in Soils and Uptake by Plants. A Selected, Annotated Bibliography. ORNL-EIS-75-77.

Gera, F. 1975. Geochemical Behavior of Long-Lived Radioactive Wastes. ORNL-TM-4481.

Martin, F. M., C. T. Sanders and S. S. Talmage (eds.). 1974. Environmental Aspects of the Transuranics. A Selected, Annotated Bibliography. ORNL-EIS-74-21 (Suppl. 3).

Routson, R. C. 1973. A Review of Studies on Soil-Waste Relationships on the Hanford Reservation from 1944 to 1967. BNWL-1464.

Scheffler, K., U. Riege, K. Louwrier, Hj. Matzke, I. Ray and H. Thiele. 1977. Long Term Leaching of Silicate Systems: Testing Procedure, Actinides Behavior and Mechanism. KFK 2456. EUR 5509e, p. 29.

Schneider, K. J. and A. M. Platt (eds.). 1974. High-Level Waste Management Alternatives. BNWL-1900, Volume I, Appendix 2.D, pp. 2.D.7-2.D-8, 2.D.21-2.D.22.

SECTION 2

PROCESSES INFLUENCING RADIONUCLIDE MOBILITY AND RETENTION

This section is concerned with a general discussion of some of the factors that are expected to influence the radionuclide-geologic media interactions. All of the factors discussed here may or may not influence the behavior of a specific element. The influence of these factors on various selected elements is the subject of the next section. The main purpose of this section is to:

1) briefly enumerate the factors and processes involved in radionuclide-geologic media interactions in the next section,
2) define various terms, and
3) outline the reasons for developing, limitations and the method of construction of various solid phase and solution species diagrams presented in the next sections.

NATURAL SOIL AND ROCK DISTRIBUTIONS

It is important to determine the concentration of the stable isotopes of a given element in the soils and rocks because the chemical behavior of the stable isotopes would not differ from that of the radioisotopes of the same element. Hence, the presence of stable isotopes can affect the mobility and retention of the radioisotopes. For example, limestone contains an average of 610 ppm strontium. Disposal or an accidental spill of ^{90}Sr-containing waste in a limestone area would very likely add much less strontium to the environment than was already present as stable isotopes. The stable isotopes of strontium can be present in such abundance that they control the soil reactions and mobility of the radioactive strontium.

The average elementary abundances in rocks and soils are given in the next section. The actual elemental concentrations may range widely from the average values given due to local conditions. It is always necessary to establish local base level concentrations to avoid disposal or storage of the radioisotope of an element in environments with high concentrations of stable isotopes of the same element. Such an environment could enhance mobility of the radionuclide.

SOLID PHASE AND SOLUTION SPECIES

Among factors that influence radionuclide behavior in the environment, the nature of the solid phases and solution species of the radionuclide is one of the most important. Through their precipitation and dissolution solid phases would cause changes in solution concentration which, in turn, would affect adsorbed ions. The environmental concentration of most radionuclides is expected to be low so that discrete solid phases of the element may not be present in the terrestrial environment. In this case the element may be distributed throughout the soil and rock matrix and adsorption reactions may control solution concentrations. However, if the concentration of the element in solution is such that a solid phase of the element can precipitate, the knowledge of this solid phase and solution ions would help in predicting the solution concentrations available for transport (Dutt, Shaffer, and Moore, 1972; Jurinak and Medrano, 1974; Rai and Franklin, 1973; Tanji and Doneen, 1966). Granted the importance of the total solution concentrations of the element, the nature of the predominant solution species are important since they affect 1) adsorption through their charge; 2) adsorption because of changes in the nature of the species due to alteration in solution properties such as pH, Eh, competing ions and complexing ions; 3) movement through the soil and rock matrix because of their physical size; and 4) plant uptake.

Laboratory information on possible solid phase and solution species of elements of interest in radioactive waste is almost nonexistent. What little information is available is very site and solution specific with such poorly defined systems that no extrapolations can be made to other situations. In order to bridge this gap, thermodynamic data are generally used to construct Eh-pH diagrams to predict stable phases and solution species (Pourbaix, 1966; Garrels and Christ, 1965). This approach also has several limitations, but is the best method until extensive laboratory data become available. Some of the limitations of a theoretical approach are:

1. The reliability of the prediction is dependent upon the accuracy of the thermodynamic data which, in a large number of elements of concern in radioactive waste, contain a large error term.
2. The approach is limited to those compounds for which information is available at the present time.
3. This approach does not consider the kinetics of reactions.
4. The predictions apply only under equilibrium conditions.
5. The influence of organic ligands and colloids which may be very important cannot be evaluated because the thermodynamic data are lacking.

In order to develop solid phase-solution species diagrams, accurate values of the equilibrium constants of all the reactants and products are required. The time and money available for this study allowed neither an extensive search nor a critical evaluation or tabulation of the available thermodynamic data. In a related DOE sponsored document, Rai and Serne (1978), the equations and thermodynamic data used to construct the solid phase-solution species diagrams are tabulated. Therefore, equilibrium constants were selected from several readily available sources, the most important of these sources being Sillen and Martell (1964); NBS publications (Rossini et al., 1952; Wagman et al., 1968, 1969, 1971; Parker et al., 1971; Schumm, 1973), Latimer (1952); Pourbaix (1966); Cleveland (1970); Keller (1971); Burney and Harbour (1974); and Baes and Mesmer (1976). The thermodynamic data were used to develop equilibrium constants for chemical equations that describe the behavior of various species. Generally these equations are used to develop Eh-pH diagrams (Pourbaix, 1966; Garrels and Christ, 1965) that provide the information regarding the stable compounds and solution species in the whole range of pH and Eh. However, Eh-pH diagrams can be used only for elements that exist in more than one oxidation state, and these diagrams do not indicate the total amount of the element and the relative amount of various species in solution under specified conditions. Therefore, activity-pH diagrams rather than Eh-pH diagrams were developed. The solid phase-solution species diagrams of elements affected by oxidation-reduction were developed at an assumed partial pressure of oxygen (0.2 atmospheres in most cases). However, the changes in solution concentration or the stability of the solid phases that would occur due to the decrease in oxygen pressures are also discussed. This approach is similar to the one used by Lindsay (1972), Baes and Mesmer (1976), and Rai and Serne (1977).

Uncomplexed, Mononuclear and Polynuclear Solution Species

An element in solution can exist as free ions or as mononuclear and polynuclear species (complexed). The total concentration of the element in solution can be obtained by summing the concentrations of all the free and complexed ions. Mononuclear species are of the type ML, ML_2, ML_3....ML_n, where M is the metal ion and L is the complexing ligand such as CO_3^{2-}, HCO_3^-, F^-, NO_3^-, Cl^-, OH^-, CN^-, $C_6H_5O_7^{3-}$ (citrate) and $C_2H_3O_2^-$ (acetate). Some examples of mononuclear species are $CoOH^+$, $Co(OH)_2^{\circ}$, $Co(OH)_3^-$ and $Co(OH)_4^{2-}$. Polynuclear species are of the type M_mL_n, where m and n are integers. Some examples of polynuclear species are Co_2OH^{3+} and $Co_4(OH)_4^{4+}$.

In general, mononuclear species of the type ML maintain higher concentrations in equilibrium with metal ions than the ML_2....ML_n species. Hence, in most cases mononuclear species of the type ML_2....ML_n do not contribute significantly to total metal ion solution concentrations. Hydroxide bridging is apparently responsible for polynuclear species of M(II), M(III) and M(IV) ions (Baes and Mesmer, 1976). The polyanions of M(V) and M(VI) usually involve oxygen bridging. In most cases, the polynuclear species do not contribute significantly to total metal ion solution concentrations.

Polymerization of a radionuclide is a special case of hydrolysis and precipitation, and is primarily a function of Eh, pH, temperature, radionuclide concentration and the presence or absence of complexing ligands. For example:

1) Pu(IV) polymerizes but Pu(VI) and Pu(III) do not significantly polymerize (Cleveland, 1970),
2) at 10^{-5}M Pu(IV), 91% of the plutonium was present as polymer at pH 8.5 (Lindenbaum and Westfall, 1965), but true colloid was not present at pH values of <7.5 for 10^{-8}M Pu(IV) (Grebenshchikova and Davydov, 1961), and

3) the presence of complexing ligands such as F^-, SO_4^{2-}, and oxidizing agents, reduce the polymerization of plutonium (Cleveland, 1970).

The metal ions of interest in this study that might be expected to polymerize include americium, antimony, cerium, cobalt, curium, europium, plutonium, promethium, ruthenium, thorium, uranium and zirconium. Usually the polymeric units are colloidal in size range ($\sim$10 Å to 10,000 Å) and possess a surface charge that tends to keep the units from coagulating and precipitating from solution. Rhodes (1957b) showed with laboratory studies of Kd versus solution pH that ^{239}Pu, ^{106}Ru, ^{95}Zr-^{95}Nb and ^{144}Ce Kd values all tended to diminish in the pH region of 9 to 13, probably due to reduced surface change on the polymers produced by the increasing amounts of NaOH added to reach the higher pH values, resulting in reduced polymer adsorption by the soil. Prediction of whether or not colloidal size polymeric units will form during a precipitation reaction and remain stable in solution is difficult because of the large number of system variables that effect possible polymer formation. However, the metal cations with high charges (M^{3+}, M^{4+}) show the greatest tendency to form polymers.

The stability constants that were available in the literature, and applicable to the soil and rock environments selected, were utilized in this study to estimate solid phases and solution species equilibria. It is unfortunate that reliable hydrolysis constants are not available for many of the elements including plutonium. Also missing are reliable formational constants for many other complex ion species such as the nitrosyl ruthenium complexes. In some cases, there is a reasonable doubt as to the identity of some of the species, including those formed with organic materials found in many soils and surface waters.

Construction and Interpretation of the Diagrams

The details of the method of constructing the diagrams presented in this report can be found in Rai and Lindsay (1975) and Rai and Serne (1977). In these diagrams the $pCO_2(g)$, K^+, and pNa^+, etc., refer to the negative logarithm of the activity (in moles/l for solution species and atmospheres for gases). The oxidation-reduction conditions are denoted by partial pressures of oxygen.

In the solid phase diagrams, any compound that lies below another compound at a given pH is the more stable. Thus, for any two solids at a specific pH, the solid that maintains lower ionic activity is more stable. In addition to stability, information regarding weathering and formation can also be obtained from these diagrams. If, in a given soil, the soil solution composition is below the solid line, the soil is under-saturated with respect to the solid represented by the line, and the mineral will dissolve or weather. On the other hand, if a soil solution point is above the solid line, the soil is supersaturated with respect to the mineral represented by the line, and the mineral can precipitate.

The solution species diagrams were developed assuming an oxidation-reduction environment, an equilibrium with a compound, and ionic activities of various cations (Ca^{2+}, Na^{+}, NH_4^{+}) and anions (Cl^{-}, HCO_3^{-}, CO_3^{2-}, NO_3^{-}, F^{-}, SO_4^{2-}, and PO_4^{3-}) that may be present in the terrestrial environment. As mentioned earlier, the organic ligands and colloids that may be present in the solutions were not considered. The solution species diagrams depict anionic, cationic, and several neutral or uncharged species for which the data were available.

ION EXCHANGE

Ion exchange is a reversible interchange of ions between two compounds, one of which is insoluble in the medium in which the exchange is carried out (Amphlett, 1964). It is one of the most common mechanisms responsible for radionuclide adsorption on geologic materials.

If X^{-} is a solid, negatively-charged medium, an exchange reaction can occur between two cations, A^{+} and B^{+} as follows:

$$X^{-}A^{+} + B^{+} \rightleftarrows X^{-}B^{+} + A^{+}.$$

The anion does not enter into the reaction in this case because the solid medium has a residual negative charge that is inherent in the mineral framework. In the case of clay minerals and zeolites, the negative charge is acquired by substitutions of Al^{+3} for Si^{+4} in the mineral lattice.

A selectivity quotient or constant can be experimentally derived from contacting the exchange medium, based in cation A^+, with a known concentration of cation B^+. For univalent-univalent cation exchanges, the selectivity coefficient,

$$K_A^B = \frac{[X^-B^+]\,[A^+]}{[B^+]\,[X^-A^+]} ,$$

where the brackets denote solution and solid medium concentrations. For a univalent-divalent exchange, the reaction would be $2X^-A^+ + B^{+2} \rightleftarrows (X^-)_2B^{+2} + 2A^+$, with the rational selectivity coefficient,

$$K_A^B = \frac{[X_2^- \, B^{+2}]\,[A^+]^2}{[B^{+2}]\,[X^-A^+]^2} .$$

If the capacity of the solid medium is known in meq/g (m_o) and the initial solution concentration in meq/ml (C_o), a relationship between the selectivity coefficient, K_A^B, and a distribution coefficient for B^+, KdB, can be derived. Assuming that $[A^+] + [B^+] = C_o$ and $[X^-A^+] + [X^-B^+] = m_o$ then

$$K_A^B = \frac{[X^-B^+]\,[A^+]}{[B^+]\,[X^-A^+]} = \frac{[X^-B^+]\,(C_o - [B^+])}{[B^+]\,(m_o - [X^-B^+])} = \mathrm{KdB} \cdot \frac{C_o - [B^+]}{m_o - [X^-B^+]} .$$

If B^+ is a trace component ($[B^+]$ much less than C_o, $[X^-B^+]$ much less than m_o), then the above can be written as:

$$K_A^B \approx \mathrm{KdB}\,\frac{C_o}{m_o} \quad \text{and} \quad \mathrm{KdB} \approx K_A^B\,\frac{m_o}{C_o} ,$$

or the Kd is inversely proportional to $[A^+] + [B^+]$. If Kd were plotted versus log $[A^+]$, a straight line would result with a slope of minus one. A divalent cation, A^{+2}, would yield a slope of minus two when plotted in the above manner. The same treatment applies equally well to anion exchange reactions.

One of the key parameters in the above treatment is the requirement that the component for which the Kd value is determined be present in the system in trace quantities. In practice, a trace quantity should be defined experimentally by determining Kd values at several concentrations of the traced ion. The Kd will remain constant, all other things being equal, over the traced ion concentration range for which the Kd concept remains valid.

An implied limitation can be found in the original exchange reaction, $X^-A^+ + B^+ \rightleftarrows X^-B^+ + A^+$. The expression requires that the solid medium, X^-, be based in cation A^+ before contacting the solution containing B^+. A Kd value that has been experimentally determined for cation B^+ without first basing the solid medium (soil, clay mineral, zeolite) in cation A^+, has been determined for an undefined system. Also, because the dimensions of m_0 were meq/g, and of C_0, meq/ml, the dimensions of the Kd value are ml/g.

If the selectivity quotient is modified with the activity coefficients for A and B on the solid medium, f_A and f_B, and in the solution γ_A and γ_B, a rational thermodynamic equilibrium constant, K, can be derived (Gaines and Thomas, 1953):

$$K = K_A^B \frac{f_B \, \gamma A}{f_A \, \gamma_B}$$

The thermodynamic quantities are sometimes of value in establishing and studying reaction mechanisms, but are limited in practical applications. The distribution coefficient (Kd) and the selectivity quotient (K_A^B) where trace concentrations are exceeded are experimentally determined values that are characteristic of a given exchange system, and can be applied in several practical situations.

Ion Exchange Properties of Soil and Rock Components

As far as soils, sediments and altered rocks are concerned, ion exchange means chiefly cation exchange. The soil particles have an amphoteric character, but in general they carry a net negative charge (Winklander, 1964). For cation exchange, the negative charge on the soil colloids increases with rising pH. The positive charge tends to increase with diminishing pH, giving rise to an anion exchange capacity on the acidic side. Chloride and sulphate ions, for example, show no adsorption at pH 7 on kanditic or smectitic soil minerals (Mattson, 1931). Lowering of the pH activates basic groups, R-OH, to $R\text{-}OH_2^+$, with the OH originating in clay mineral broken bonds and hydrous oxides of iron, aluminum and manganese. They take part in exchange reactions such as, $R\text{-}OH_2^+Cl^- + NO_3^- \rightarrow R\text{-}OH_2^+ NO_3^- + Cl^-$. However, the anion exchange capacities of most soils are relatively minor compared to their cation exchange capacities because the pH of most soils is seldom as low as 4.0, and the number of sites that can be activated to function as anion exchange sites usually are relatively small as well.

There are at least two types of anion exchange in clay minerals. The first involves replacement of the hydroxyl (OH^-) ions by other anions. McAuliffe et al. (1947) showed that the OH ions of clays can enter into exchange reactions by using clays with deuterium-tagged hydroxyls. The replacement of hydroxyls by fluoride ions also was reported (Dickman and Bray, 1941).

Another type of anion exchange involves the substitution of anions such as phosphate, arsenate and borate on the edges of the (SiO_4) (silica tetrahedron) sheets, perhaps growing as extensions of these sheets. Other anions such as sulfate, nitrate and chloride are not adsorbed because their geometries are not comparable to the silica tetrahedra.

A third type of anion exchange site could occur as a positive site on basal surfaces as a result of a local electrostatic imbalance in the clay framework such as an excess of aluminum in the octahedral position.

In the cases of both OH ion replacement and anion exchange due to geometrical similarities between the anion and silica tetrahedra, exchange would occur around clay mineral edges. There would be very little exchange on basal surfaces of expandable clay minerals. Investigations of anion exchange are difficult because of the low pH requirement. However, for clay minerals the cation and anion exchange capacities should be about equal at optimum pH values for each.

The anion exchange capacities of expanding clays were 12 to 31 meq/100 g for smectites and 4 meq/100 g for vermiculite, while kandites varied from 6 to 20 meq/100 g (Hofmann et al., 1956). Compare these anion exchange capacity data with those of Table 2-1 for cation exchange at pH 6 to 8.

The cation exchange capacity ranges of some common clay minerals are given in Table 2-1. The ranges vary due to differences in crystallinity and particle size. In soils, rocks, weather rocks and sediments, cation exchange capacities are due mainly to the types and quantities of minerals in the silt (2 to 62 µm) and clay (<2 µm) size fractions.

TABLE 2-1. CATION EXCHANGE CAPACITIES (CARROLL, 1960, 1970)

Mineral	Cation Exchange Capacity, meq/100g
Kaolinite	3-15
Halloysite ($2H_2O$)	5-10
Halloysite ($4H_2O$)	40-50
Smectites	36-100
Illite	10-40
Vermiculite	100-150
Chlorite	4-47
Glauconite	11-20
Palygorskite	20-30
Allophane	70
Zeolites	100-300
Organic Matter in Soils	130-350
Feldspar	<1
Quartz	<1

There is a considerable variation in cation exchange capacity with particle size shown by the non-expandable soil clays. Kaolinite, for example, shows an increase in exchange capacity as outlined in Table 2-2. The expanding layer silicates, on the other hand, show little change in cation exchange capacity with particle size as shown for some smectites in Table 2-3.

TABLE 2-2. INCREASE IN CATION EXCHANGE CAPACITIES WITH KAOLINITE PARTICLE SIZE (HARMON AND FRAULINI, 1940)

	Particle Size, µm						
	10-20	5-10	2-4	1-0.5	0.5-0.25	0.25-0.1	0.1-0.05
Cation Exchange Capacity, meq/100g	2.4	2.6	3.6	3.8	3.9	5.4	9.5

TABLE 2-3. INCREASE IN CATION EXCHANGE CAPACITIES FOR SOME SMECTITES WITH PARTICLE SIZE (CALDWELL AND MARSHALL, 1942)

		Particle Size, μm				
Cation Exchange	Smectite	2-1	1-0.5	0.5-0.2	0.2-0.05	-0.05
Capacity, meq/100g	Nontronite	60.8	61.0	64.3	5.70	-
	Saponite	69.3	76.0	8.15	86.3	81.4

An increase is to be expected with decreasing particle size when the cation exchange capacity primarily occurs from broken bonds in minerals such as illite and kaolinite. In the case of expanding layer silicates where most of the capacity is on basal plane surfaces, particle size has little effect on cation exchange capacity.

Excessive grinding of clay and nonclay minerals causes an increase in cation exchange capacity, probably a result of the same decrease in particle size and number of broken bonds, as shown in Table 2-4. A rubber-lined ball mill and polished agate balls were used for the grinding.

TABLE 2-4. CATION EXCHANGE CAPACITY IN meq/100 g DUE TO GRINDING (KELLY AND JENNY, 1936)

		Grinding Time, Days		
	100 Mesh	2	3	7
Muscovite	10.5	-	76.0	-
Biotite	3.0	62.0	72.5	-
Kaolinite	8.0	57.5	70.4	100.5
Montmorillonite	126	-	238.0	-

The clay minerals are relatively sensitive to pH. Chatterjee and Paul (1942) and Mukherjee et al. (1942) have shown that so-called hydrogen clays are really hydrogen-aluminum or hydrogen-magnesium-aluminum systems, the magnesium and aluminum being removed from the clay framework with resulting clay damage. Other things being equal, higher valence cations more easily replace lower valence cations, and are more difficult to replace when already present on a clay or zeolite. Hydrogen ions are an exception because they behave more like divalent or trivalent cations. With ions of the same valence, the smaller diameter hydrated cations are more tightly held than the larger diameter hydrated cations. The usual lyotropic replacement series on smectites, for example, is $Cs^+ > K^+ > Na^+ > Li^+$ and $Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2}$. An exception arises when the cation just fits the size and charge requirements of the anionic site, as does K^+ into the basal sites of illite.

These cations can cause structural modifications in the clay or zeolite structure that leads to their so-called "fixation" (Bray and DeTurk, 1939; Wood and DeTurk, 1941; Nishita et al., 1956; Frysinger, 1960; Tamura and Jacobs, 1960; Tamura and Jacobs, 1961).

In contrast to clay minerals, soil organic matter has no well-defined ability to bind exchangeable cations, although the exchange displacement follows the lyotropic order, as do most of the clays (Bartlett and Norman, 1938). The cation exchange capacity increases with increasing pH values, arising from the increasing dissociation of phenols and carboxylic acids at higher pH levels (Broadbent and Bradford, 1952).

The cation exchange capacity of soil organic substances are reported as between 150 and 450 meq/100 g depending on the origin of the fractions. Posner (1966) showed that the cation exchange capacities of humic acids extracted from a red-brown soil under different conditions yielded substances with relatively similar cation exchange capacities. Yields of humic acids varied from 2.7 to 12.0 g/kg soil and cation exchange capacities varied from 217 to 409 meq/100 g, with the averages at 7.0 g/kg soil for yield and 310 meq/100 g capacity. Cation exchange isotherms between humic acids and alkaline earth and alkali metals were investigated in detail by Zadmard (1939). The role of carboxyl and hydroxyl groups in metal cation fixation by organic soil materials was investigated by Schnitzer and Skinner (1965). Specific blocking of the functional groups indicated two reaction types: 1) a main reaction with participation of both carboxyl and phenolic groups, and 2) a lesser reaction involving only carboxyl groups. No evidence was found for exchange reactions of the carbonyl groups.

ANION EXCLUSION

Reactions between an inorganic anion and a soil or rock exchanger can involve both adsorption and repulsion. Adsorption of anions is due to a limited number of positive charges on soil minerals (anion exchange capacity). Anion exchange and the capacities of various minerals are discussed in the ion exchange section above. Anion exclusion involves the repulsion of anions by the predominantly negatively charged clay minerals and zeolites in soil (Schofield, 1947; de Haan and Bolt, 1963; de Haan, 1964; de Haan, 1965). The higher the cation exchange capacity (negative charge) of the soil or rock, the more pronounced the anion exclusion (Thomas and Swoboda, 1970). The high cation exchange capacity smectites exhibit anion exclusion to a greater degree than do the kandites (kaolinite group). Thus anions, such as chloride, iodide and pertechnetate, can be repelled by the negative charges of a high cation exchange capacity soil into the higher velocity soil solution flow channels and break through the soil column in less than one pore volume of displacing solution (Thomas and Swaboda, 1970; Cassel et al., 1975). The implication for anionic radionuclides and anionic complexes of radionuclides is that their displacement through high cation capacity soil columns can take place at less than one displacing solution volume, with a higher apparent migration velocity than the displacing solution.

DIFFUSION

One of the parameters of aqueous transport of ions is that of aqueous diffusion. The transport of matter in the absence of bulk flow is referred to as the process of diffusion. The flux of matter due to diffusion is proportional to the concentration gradient and is a molecular process. In general terms, the flux, J_{iz}, of component i in the z direction, is (Fick's first law) $J_{iz} = -D\frac{dn_i}{dz}$, where D is the proportionality constant and diffusion coefficient, with the dimensions of cm^2/sec, J_{iz} has the dimensions of moles/cm^2/sec, n_i is the concentration of material i and the negative sign indicates that flow of material i in the z direction is also in the direction of lower i concentration. In a binary electrolyte, at infinite dilution, the aqueous diffusion coefficient is:

$$D_o = \frac{2\mu_1 \mu_2 RT}{(\mu_1 + \mu_2) F} ,$$

where μ_1 and μ_2 are the mobilities of the two ions (K^+ and Cl^-, for example, as a binary electrolyte former), RT is the gas constant times the degrees Kelvin and F is a faraday. The dimensions of D_o are once again cm^2/sec. The ionic mobilities of many ions are known (Harned and Owen, 1958; Dean, 1973) in aqueous solutions. Scott et al. (1974) defined an apparent or measured difusion coefficient (D_A) and its relation to the aqueous diffusion coefficient (D_o) as (the change of concentration with time in the x direction)

$$\frac{\partial C}{\partial t} = \frac{D_o}{R} \frac{\partial^2 C}{\partial x^2} ,$$

where R is a retardation factor.

The retardation factor, R, was defined as

$$R = 1 + \frac{\rho}{\varepsilon} Kd$$

where ρ is the soil bulk density, ε is the pore fraction (volume occupied by the solution phase) and Kd is the equilibrium distribution coefficient with dimensions of ml/g. Note that the above expression is the same one that is used to evaluate the relationship between groundwater velocity and radionuclide migration velocity. The same retardation factor serves in both cases. The apparent diffusion coefficient is defined by $D_A = D_o/R$.

Relyea (1977) obtained D_o values for 10^{-8}M plutonium nitrate in 0.01M HNO_3, 0.1M KNO_3 and 1M $Ca(NO_3)_2$ of $4.8 \times 10^{-6} \pm 2.5 \times 10^{-6}$ cm^2/sec, $7.8 \times 10^{-5} \pm 3.7 \times 10^{-5}$ cm^2/sec and $3.0 \times 10^{-5} \pm 2.0 \times 10^{-5}$ cm^2/sec, respectively. These D_o values may be compared to the limiting diffusion coefficient of KCl, for example, of 2.0×10^{-5} cm^2/sec. Subsequent measurement of the plutonium particle size in the 0.01M HNO_3 by means of the Stokes-Einstein equation showed that it had rapidly hydrolyzed to particles about 8 Å in diameter at 25°C. Increasing the nitric acid level to 0.1M reduced the effective radius of plutonium particles to less than 1 Å. The measured D_o from the Fuquay soil supernate was $2.7 \times 10^{-5} \pm 1.2 \times 10^{-5}$ cm^2/sec at pH 2.0, 25°C and 8×10^{-10}M plutonium nitrate, and from the Burbank soil at pH 7.1 and plutonium 5×10^{-11}M,

$D_o = 3.6 \times 10^{-6} \pm 1.0 \times 10^{-6}$ cm^2/sec. The effective plutonium radius for the Burbank sample was 6 Å. The D_o values of various molecules are remarkably similar in the absence of polymerization, or some other complicating factor. The plutonium D_A values obtained by Relyea for the Burbank sandy loam at $\varepsilon = 0.30$, T = 21°C and 791 hours was 5×10^{-10} cm^2/sec and at $\varepsilon = 0.14$, T = 21°C and 3600 hours was 8×10^{-11} cm^2/sec. The above D_A values can be compared to the previously-given D_o value for Burbank supernate to illustrate the influence of the retardation factor (and Kd) on the mobility of high Kd radionuclides. If, on the other hand, the radionuclide Kd value is very low, the apparent diffusion coefficient (D_A) approaches the aqueous diffusion coefficient (D_o) in value.

The simple expression, $\bar{x} = \sqrt{Dt}$ (Jost, 1960) can be utilized to determine the effect of D, the diffusion coefficient and t, time, on the distance (root mean square distance) that a radionuclide will migrate. The dimension of D is cm^2/sec and t also is in seconds with x in cm. If D_A is substituted for D in Jost's expression above, it can be seen that the high Kd radionuclides such as plutonium must have very high t values in order to diffuse a significant distance. However, the low Kd value radionuclides such as tritium or technitium, can diffuse distances of up to 25 cm/yr, due to D_A values of close to 1×10^{-5} cm^2/sec. Diffusion can be an important migration mechanism for the low Kd radionuclides. Its potential contribution to migration should be examined for each radionuclide.

REPLACEMENT REACTIONS

Replacement is a type of precipitation reaction in which one of the ions of a final replacement product is contributed by a solid that is more soluble in the contacting solution than is the final product. Replacement reactions can be divided into two kinds: 1) anion replacement reactions in which only the anion in the solid is replaced by an anion in solution, with cations of both solution and solid being common, and 2) cation replacement reactions in which only the cation in the solid is replaced by the a cation in solution, with anions of both solution and solid being common. Some examples of anion and cation replacement reactions are given in Table 2-5. The principle governing replacement reactions, assuming that the solution-solid system obeys Raoult's law, is a relatively simple solubility relationship.

TABLE 2-5. EXAMPLES OF REPLACEMENT REACTIONS (AMES, 1961a; AMES, 1961b)

Original Solid	Ion in Solution	Reaction	Solid Product
		Anion Replacement	
$CaCO_3$	F^-	$CaCO_3 + 2F^- \leftrightharpoons CaF_2 + CO_3^{-2}$	CaF_2
$CaCO_3$	PO_4^{-3}	$5\ CaCO_3 + 3PO_4^{-3} + OH^- \leftrightharpoons Ca_5(PO_4)_3OH + 5\ CO_3^{-2}$	$Ca_5(PO_4)_3OH$
		Cation Replacement	
$CaCO_3$	Ba^{+2}	$CaCO_3 + Ba^{+2} \leftrightharpoons BaCO_3 + Ca^{+2}$	$BaCO_3$
$CaCO_3$	Sr^{+2}	$CaCO_3 + Sr^{+2} \leftrightharpoons SrCO_3 + Ca^{+2}$	$SrCO_3$
$CaSO_4\ 2H_2O$	Ba^{+2}	$CaSO_4 \cdot 2H_2O + Ba^{+2} \leftrightharpoons BaSO_4 + Ca^{+2} + 2H_2O$	$BaSO_4$
$CaSO_4\ 2H_2O$	Sr^{+2}	$CaSO_4 \cdot 2H_2O + Sr^{+2} \leftrightharpoons SrSO_4 + Ca^{+2} + 2H_2O$	$SrSO_4$

The difference in solubility between the original solid and replacement product is the driving force for the reactions shown in Table 2-5. The reaction will cease as the ratio of replaced anion or cation to replacing anion or cation approaches the same ratio as the activity products of the original solid and solid product with the common anion or cation. For example, if the activity products are 1.5×10^{-9} for $BaSO_4$ and 3.6×10^{-5} for $CaSO_4 \cdot 2H_2O$ during the replacement reaction $CaSO_4 \cdot 2H_2O + Ba^{+2} \leftrightharpoons BaSO_4 + Ca^{+2} + 2H_2O$, the reaction rate approaches zero as the activity ratio of Ca^{+2} to Ba^{+2} approaches $\frac{3.6 \times 10^{-5}}{1.5 \times 10^{-9}}$, or 2.4×10^4. If excess calcium is added, the equilibrium can be made to go to the left and form $CaSO_4 \cdot 2H_2O$) (gypsum). When several solid products are theoretically possible, only the least soluble will form.

Replacement reactions involve the dissolution of the original solid at an interface between solid product and original solid (Ames, 1963). Bonds between cation and anion in the original solid must actually be broken, the ions diffuse into solution and recrystallize on the advancing solid product. Ions must be able to diffuse through the solid product to the reaction face or the replacement reaction soon ceases. It is during the portion of the reaction when ions are traveling between the more soluble original solid to the less soluble final product that trace radionuclides able to satisfy the ion size and charge requirements of the final product are included in the growing reaction product (Ames, McHenry and Honstead, 1958; Ames, 1959; Ames, 1960). Replacement type reactions that removed ^{90}Sr from high salt wastes containing 0.01M PO_4^{-3} were first reported by Rhodes (1957). The presence of the phosphate in the solution caused a reaction with the calcite in the soil to form apatite, $Ca_5(PO_4)_3OH$, with the ^{90}Sr substituted for calcium in the apatite crystal lattice. Other cations that can be included in the apatite lattice during the replacement reaction include promethium, uranyl ions and plutonium (Ames, 1960). The cations that are removed into the crystallizing apatite are also the cations found to be enriched in natural apatites, including strontium, uranium, the rare earths, thorium, manganese and barium (Deer, Howie and Zussman, 1962). The effects of phosphate concentration, calcite replacement rate and pH on removal of ^{90}Sr from solution was given by Ames (1959). Tamura (1962) showed the effects of contact time and phosphate concentration on ^{90}Sr removal by calcite replacement. Belot and Gailledreau (1963) studied the kinetics of ^{90}Sr retention during the calcite-phosphate replacement reaction.

One of the problems with the use of replacement type reactions for radionuclide removal from waste solutions involves kinetics. As mentioned above, the reaction is diffusion-controlled. As the thickness of solid product becomes greater, the diffusion path becomes longer and more tortuous, leading to increasingly slower reaction rates. If the solid product coating is too thick, reaction ceases and the radionuclides pass through the soil without removal by a replacement reaction. In addition, it is usually necessary to add a substantial amount of reacting ions such as phosphate to the waste solution before ground disposal, which can be costly and lead to a precipitate in the solution prior to disposal. Adjustment of solution pH also may be required, as in the case of the calcite-phosphate reaction.

PHYSICAL TRANSPORT AND FILTRATION

Colloidal particles, due to their large size compared to solution species and their changes in charge in response to pH, exhibit different migration and retention behavior from solution species (Van Olphen, 1963; Grebenshchikova and Davydov, 1965; Sheidina and Kovarskaya, 1970). Colloidal radionuclide particles that have been described in the literature are of two types. These are true colloids and pseudocolloids. A true colloid is defined as composed of a radionuclide only, while a pseudocolloid is a radionuclide adsorbed on another colloidal size particle. Several rare earths, zirconium, plutonium, curium, antimony and americium could occur partially as true colloids, precipitates or particulate suspensions (Rhodes, 1957; Bensen, 1960; Andelman and Rozzell, 1970; Fukai and Murray, 1974; Price and Ames, 1975; Ames, 1976). The downward movement of colloidal particles through soils would mainly depend upon physical factors such as permeability, rate of water movement and particle size. This same dispersion and translocation of soil colloids occurs under natural soil conditions (Drew, 1967; Gerasimov and Glazovskaya, 1960) and may lead to problems with internal soil drainage. Ground disposal of low ionic strength condensate wastes was reported by Routson (1973) to result in partial plugging of the soil column and reduced infiltration rates because of dispersion and filtration of upper soil colloids. Generally, the downward movement would be limited because the colloids are subjected to filtration by the soils and sediments (Routson, 1973; Price and Ames, 1975; Ames, 1976). The lateral or horizontal movement of colloidal particles depends upon their degree of exposure to wind and surface water action (Hakonson et al., 1975).

A recent report concerned with the long term leaching of silicate glasses containing high level waste (Scheffler et al., 1977) serves as an example of physical transport of several actinides. The base glass composition used to contain the radionuclides was SiO_2 = 50.5 wt%, TiO_2 = 4.2 wt%, Al_2O_3 = 1.4 wt%, B_2O_3 = 13.6 wt%, CaO = 2.8 wt% and Na_2O = 27.5 wt%. Two actinide-containing glasses were made using the base glass formula. One contained 78.43 wt% base glass, 16.64 wt% fission product and corrosion product oxides, 4.90 wt% AmO_2 and 0.03 wt% CmO_2. The other glass contained 80.85 wt% base glass, 17.15 wt% fission product and corrosion product oxides, 0.005 wt% AmO_2 and 2.00 wt% PuO_2. Leaching experiments with distilled water, 1M NaCl and a saturated brine solution were performed. Actinide concentrations were on the order of 10^{-9}M in the leachates after a period of initial leaching, with rates of 10^{-6} to 10^{-7}g/cm^2/day common. An examination of the leachate to determine the form of the actinides indicated that particles attached to the actinides actually dissolved from the glass rather than the actinides alone, and that the particles were high silica polymers with an average size of 10^{-2} μm. The actinides (curium americium, and plutonium) were bonded to the silica polymers in the glass and remained so in the leachate.

SATURATION EFFECTS

In migration of radionuclides, hydraulic conductivity is of primary importance. Hydraulic conduction is the ratio of the flux density (the volume of water flowing through a cross-sectional area per unit time) to the hydraulic gradient (the head drop per unit distance in the flow direction). The reason for the importance of hydraulic conductivity to radionuclide migration is the requirement that a liquid (water) move the radionuclides either physically as dispersed colloids or on dispersed soil colloids, or as ions or neutral complexes in solution. If the soil water does not move, then the radionuclides in, or contacted by, the soil water do not move except by diffusion, a relatively slow process (Hajek, 1965; Hajek, 1966; Rancon, 1973).

Coincidentally, the most important difference between saturated and unsaturated flow is the same hydraulic conductivity (Hillel, 1971). When the soil is saturated, nearly all pores are filled and conducting, and conductivity is at a maximum. As the soil becomes unsaturated, some of the pores become air-filled and the conductive cross-sectional area decreases. In addition, the first pores to empty under tension are the largest and most conductive, and tortuosity is increased by these empty pores. In unsorted soils and sediments, the large pores that resulted in high conductivity at saturation become barriers to liquid flow between smaller pores during unsaturated flow. Hence, the transition from saturated to unsaturated flow may result in a steep drop in hydraulic conductivity of several orders of magnitude as the tension increases from 0 to 1 bar. At higher tensions, conductivity may be so low that steep negative pressure gradients are required for any appreciable soil water flow to occur.

An interesting corollary of the pore size-conductivity relationship is that at or near saturation, a sandy soil conducts water more rapidly than a clay soil with many micropores. When the soils are unsaturated, however, many of the micropores in the clay soil remain filled, and consequently, the hydraulic conductivity in the clay soil does not decrease nearly as sharply as it does in sandy soil under the same tension. In fact, an occurrence of a sand layer in a clay soil can constitute a barrier to water flow through the clay soil under unsaturated flow conditions (Hillel, 1971; Winograd, 1974).

Most of the work on radionuclide adsorption by soils has been on nearly saturated to saturated flow systems, mainly because saturation represents a system parameter where hydraulic conductivity, and subsequently radionuclide migration, is at a maximum value. Because most of the laboratory radionuclide adsorption work on soil columns is conducted at saturated flow conditions, and the soil-water system is largely unsaturated during waste disposal operations, Knoll (1960) examined the possibility that the cation exchange capacity of the soil under unsaturated flow conditions was not equal to the soil capacity at saturated flow conditions. His interest was in applying laboratory results to field situations. Small columns of a fairly uniform, very fine sand at constant temperature, packed bed density and tension were used with an influent solution containing 1.0 g/l Ca^{+2}, 0.1 mg/l Sr^{+2} and 2×10^{-2} μCi/ml ^{90}Sr. The results of the experiments are given in Table 2-6. There was apparently no difference in strontium capacity between saturated and unsaturated flow conditions.

TABLE 2-6. SOIL CAPACITIES FOR SATURATED AND UNSATURATED FLOW CONDITIONS (KNOLL, 1960)

% Saturation	Average Flow Rate, ml/hr	Strontium Capacity, meq/100 g
100	1.3	4.0×10^{-4}
100	2.5	4.4×10^{-4}
100	10.3	5.2×10^{-4}
100	11.0	5.2×10^{-4}
100	10.2	4.6×10^{-4}
65	2.1	3.6×10^{-4}
65	1.42	6.0×10^{-4}
58	0.22	5.2×10^{-4}
48	0.3	5.4×10^{-4}
36	0.2	5.4×10^{-4}

However, it is worth noting that column flow rate differences between 100% saturation and 36% saturation are less than a factor of 100. With use of an aggregate of less uniform pore size, flow rate (hydraulic conductivity) differences could have been much greater, the volume of soil contacted by the aqueous phase under unsaturated flow conditions much smaller, and hence the cation exchange capacity of soil might have differed considerably between saturated and unsaturated flow conditions. On the other hand, the clay fraction of the soil constitutes the largest exchange capacity and smallest pore sizes. Since the smaller pores are involved in unsaturated flow, there may be little obvious effect on the exchange capacity of the soil in desaturating it. If the columns are normalized by referring to a column pore volume rather than a simple effluent volume, the difference in ion exchange capacities of saturated and unsaturated flow columns tends to disappear.

Nielsen and Biggar (1961, 1962a, 1962b) have shown that the drier the soil, the greater the effluent volume required to reach a tracer effluent/influent ratio (C/Co) of 1.0. The desaturation eliminates the larger flow channels and increases the stagnant water volumes which are difficult to displace. The relatively unmoving water volumes caused by desaturation are shown as C/Co versus volume of effluent (ml)/volume of water in the column (ml). The latter coordinate represented the effluent volume divided by the pore volume used by the soil at that saturation. Desaturating the soil progressively shifted the initial breakthrough to the left and increased skewness of the breakthrough curves. Aqueous diffusion is a relatively unimportant migration mechanism near saturation, but can become important as solution velocity through the soil decreases at unsaturated flow conditions for low Kd radionuclides.

Nelson et al. (1962) conducted model field tests in disposal sites, one 24 in.^{2} and the other 6 in.^{2}. The influent was a solution of 600 ppm Ca^{+2} and ^{85}Sr. The water table at the field site was 12 ft below the ground surface, overlain by a fairly homogeneous fine sand and silt soil with 31% porosity. Only a small part of the soil beneath the model disposal site was found to be water saturated as measured by neutron moisture probe. A section through the disposal site was monitored to show moisture distribution to the groundwater table. Unsaturated flow conditions were typical of most of the section.

Baetsle et al. (1966) examined the breakthrough curves of ^{60}Co, added to the influent as $K_3\,^{60}Co\,(CN)_6$, through Mol white sand. Percolation velocity was about 3 cm/hr at soil saturation of 100%, 76%, 58% and 46%. The data were plotted as effluent volume in milliliters versus fraction of the influent ^{60}Co concentration in the effluent at a given throughput volume. The curves were somewhat different in shape than those of Nielsen and Biggar (1961) because percolation velocity was ten times faster through the ^{60}Co column, and the columns were only about one-fifteenth as large as those used by Nielsen and Biggar. The differences resulted in a flattening of the terminal ends of the ^{60}Co column breakthrough curves, and a very rapid appearance of the ^{60}Co tracer in the initial column effluents. Columns of yellow eolian sand were used to obtain ^{85}Sr breakthrough curves at 100%, 45% and 30% saturation. These columns tended to load in successive steps, indicating that the solution in the non-saturated columns percolated through preferred channels. The normalized breakthrough curves also were given for the strontium work. The normalization consisted of plotting C/Co versus the volume of effluent in cm^3 divided by the volume of water in the soil column in cm^3. The unsaturated pore volume was equal to the fraction of soil saturation times the soil pore volume at 100% saturation. Normalized curves also were given for ^{134}Cs loading on the yellow eolian sand. The stepwise loading was less pronounced but dispersion became increasingly important as the soil became less saturated.

Several hydrodynamic dispersion coefficients in the unsaturated zone were determined and these values are given in Table 2-7. The same method was used to obtain dispersion coefficients for saturated flow. After the pore volume for a given saturation was determined on the column, a thin layer of ^{131}I contaminated sand was added and the elution curve of the radionuclide obtained at the same saturation. The elution curves counted at time t were then plotted on a cumulatively linear probability scale as $\sum\frac{C/Co}{\Sigma C/Co}$ versus cm of column length. The curve on probability paper became nearly a straight line. Between the abscissa values 0.159 and 0.841, the standard deviation, σ, was determined, and using the relationship $\sigma = \sqrt{2Dt}$, the dispersion coefficient, D, was calculated. Strontium adsorption had a smaller dispersion coefficient in the less saturated columns. The velocity of percolation through the soil averaged 4 cm/day, or about 5×10^{-5} cm/sec. The authors concluded that molecular diffusion played a major role in radionuclide movement as soil saturation became a very small value. There is considerable controversy in the literature at present regarding the extension of the dispersion concept to a field scale.

TABLE 2-7. DISPERSION COEFFICIENTS IN THE UNSATURATED ZONE OF A YELLOW EOLIAN SOIL (BAETSLE ET AL., 1966)

	Soil Saturation, %					
	100	75	55	45	35	30
Radionuclide	Dispersion, cm^2/sec					
$^{131}I^-$	-	2.65×10^{-4}	1.1×10^{-3}	1.9×10^{-3}	2.5×10^{-3}	-
	-	2.20×10^{-4}	9×10^{-4}	-	-	-
$^{60}Co(CN)_6^{-3}$	3.13×10^{-4}	6.10×10^{-4}	7.4×10^{-4}	9.5×10^{-4}	1.2×10^{-3}	-
$^{85}Sr^{+2}$	-	-	-	3.3×10^{-6}	-	6×10^{-6}

Schwille et al. (1967) reported some model experiments on fluid flow in the transition zone from unsaturated to saturated soils. They stress the difficulties involved in analytically treating liquid flows even in homogeneous media, and suggest that whenever possible field tests should be used to investigate the migration of radioactive solutions.

Routson and Serne (1972), in a study involving experimental verification of their one-dimensional PERCOL model, determined the breakthrough curves and ^{85}Sr capacity for unsaturated Tank Farm sandy loam soil columns at 96%, 75%, 62% and 45% of saturation. The column volumes used were adjusted for pore volume at that saturation. The parameters are given for each column including influent solution composition, soluble salts in the initially dry soil column, $CaCO_3$ content, temperature, bulk density, flow rate, soil volume, soil weight and column dimensions. At 45% saturation, the flow rate was reduced to 0.055 cm/hr. There was no apparent reduction of capacity as a function of saturation in these systems. Obtaining curves and capacities at lower saturations would have required nearly 1 year of experimental time. At the higher tensions and lower saturation, only a very limited amount of solution would be transmitted per unit area. The fraction of the total radionuclides adsorbed during ground disposal of liquid wastes in the very low saturation zones was considered to be negligible due to the small volumes of solution per volume of soil.

Rancon (1969, 1973) performed several field studies of water behavior in unsaturated soils. Simple methods were developed to measure in situ the movements of the soil wetting front (defined as 2% H_2O by volume), the radionuclide front and the kinetics of soil drying. Rancon stated that soil contamination did not move when there was no transfer of liquid water by infiltration or redistribution, at least over the time period of the study (3 months). The wetted front always constituted the maximum envelope of the contamination, and all movement and redistribution of the radionculides took place within this limit. Iodine and strontium did not move in the soil column during soil drying by evapotranspiration. However, if the water table is shallow, a steady flow of liquid can occur from a water source below to the evaporation sink above (Hillel, 1971) as a function of the micrometeorological conditions (evaporation rate) and water transmitting properties of the soil profile. Such capillary soil moisture transmission could transport radionuclides to the surface, just as it has been known to transport salts to the surface (salinization). Without a carrier, part of the ^{131}I used became fixed in the soil during the drying out phase of the evapotranspiration studies and did not move during a following elution. Tritium was not retained in the soil under similar circumstances. The protection afforded the groundwater by unsaturated soils was emphasized.

Three breakthrough curves which might be encountered with the use of soil columns are shown in Figure 2-1 (Nielsen and Biggar, 1962b). In the first, no interactions between solid, solvent and solute have occurred. Piston flow rarely, if ever, occurs in soil columns because pores of constant radii would be required to attain it. Ion exchange resin breakthrough curves approach piston flow (Samuelson, 1963). The second curve showing longitudinal dispersion effects can be seen with soil columns under the proper operating conditions (where the solid is selective for the tracer ion and the column flow rate is very slow, reducing hydrodynamic dispersion to a minimum). This symmetrical breakthrough curve (area A = area B) can be used to derive a Kd value where $C/C_0 = 0.5$. The third type of breakthrough curve in Figure 2-1 shows that the curve is not symmetrical (area A $\neq$ area B). This curve is typical of a soil composed of equal-sized aggregates with intra- and inter-aggregate pore systems of differing size, which gives an extremely wide range in pore velocity distribution that is bimodal at saturation. In addition, the breakthrough curve can

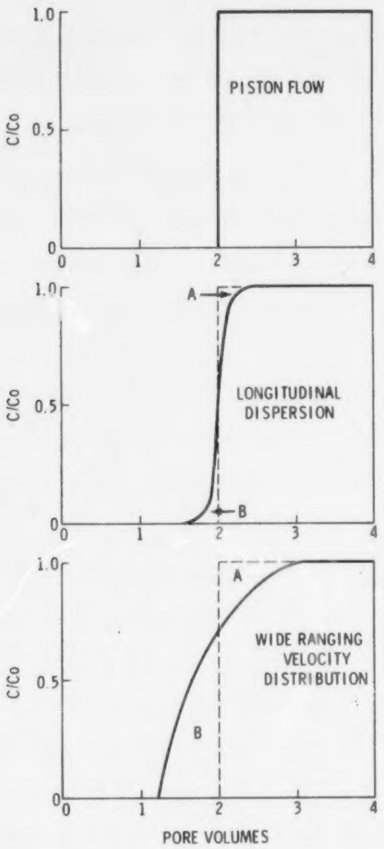

Figure 2-1. Types of column breakthrough curves (Nielsen and Biggar, 1962b)

be displaced to the right by any chemical or physical process that retains the solute within the column. Incomplete mixing throughout the entire soil solution moves the breakthrough curve to the left of a piston flow curve. In reality, the actual radionuclide breakthrough curve usually represents some combination of the five types of curves discussed above. Hence, column breakthrough data can seldom be used to accurately determine Kd values.

SPECIFIC RETENTION

Specific retention, as defined by Meinzer (1933), is the ratio between the volume of water that a soil or sediment will retain against the pull of gravity and its packed volume from an initially saturated condition. It is usually given as a percentage and can be expressed as $R = 100 (r/V)$, where R is specific retention, r the volume of water retained against the pull of gravity and V the packed volume of the soil or sediment.

Disposal on a specific retention basis of selected liquid waste solutions was practiced at Hanford from 1944 to about 1962. As used at Hanford, specific retention in practice represented the volume of liquid that could be discharged to a disposal pit of known dimensions without leakage to the groundwater. The specific retention was expressed as a percent of the soil column volume as measured by the cross-sectional area of the disposal pit bottom and the height of the soil column between water table and pit bottom. Lateral spreading was ignored to introduce a conservative element into the specific retention calculation.

A centrifugal technique for estimating soil specific retention properties was reported by Bierschenk (1959). Data were obtained indicating that the natural moisture content of Hanford soils could be reproduced by draining a 1-cm thick soil sample from the same horizon at 1000 gravities for 1 hour. The average ratio of the natural field moisture content to that of the centrifuged samples ranged from 0.82 to 1.06. The specific retention capacity of Hanford soils varied from less than 1 to 2 vol%. Usually the only reason for resorting to specific retention was because normal ground disposal methods were inadequate (Haney, 1957).

The problems associated with specific retention as a radionuclide waste disposal technique include the fact that the forces holding the radionuclide waste solution are relatively weak and that the radionuclides which are disposed by this technique often remain in the retained solution. Any water added at the top of the soil column, from natural precipitation or irrigation, would lead to the migration of the retained waste solution into the groundwater. Hence, specific retention as a waste disposal technique would be limited to arid areas where there is little downward migration of precipitation to the groundwater and no chance of other water additions to the top of the soil column. In addition, large soil volumes are required for specific retention disposal because very little of the soil column ion exchange capacity is utilized.

THE DISTRIBUTION COEFFICIENT OR Kd

One of the most useful concepts for dealing with radionuclide migration and retention processes on geologic materials is that of the distribution coefficient or Kd. The application of the Kd concept to ion exchange reactions was given above. However, the distribution coefficient can be directly derived from the same thermodynamic principles underlying ion exchange and other physicochemical reactions. The more general derivation allows the application of the Kd concept to a broad selection of radionuclide reactions with geologic media.

The distribution of a dilute solute (trace ion) between two immiscible solvents (aqueous solution and solid medium), can be derived from μ and μ', the chemical potentials of the trace ion in the solution and solid medium, respectively. At equilibrium, $\mu = \mu'$. If both are ideal dilute solutions, then $\mu = \mu^* + RT\ell nx$ and $\mu' = \mu'^* + RT\ell nx'$, and by definition, $\mu^* + RT\ell nx = \mu'^* + RT\ell nx'$, where μ^* and μ'^* are standard free energies and x and x' are the concentration of dilute solute in the solution and solid medium, respectively (Denbigh, 1971). Rearranging, $RT\ell n \frac{x'}{x} = -(\mu'^* - \mu^*)$. Then $\frac{x'}{x} = Kd$ because both μ'^* and μ^* are independent of composition. The distribution coefficient, (Kd), also is independent of the concentration of trace ion in the solution and on the soil. The quantity $\mu'^* - \mu^*$ is the standard free energy change, ΔG^*, for the reaction:

$$\text{Trace ion in solution} \rightarrow \text{Trace ion on solid medium (soil, rock)},$$
$$\text{and } RT\ell nK = -\Delta G^*,$$

which is the usual relationship for a chemical reaction. If the solute (trace ion) is very dilute, then the equilibrium mole fractions are proportional to the concentration, and Kd equals the concentration of trace ion on the solid medium divided by concentration of trace ion in solution (times a correction factor to yield a result in solution volume per weight solid medium). The Kd was originally proposed as a distribution law by Nernst in 1891 (Denbigh, 1971).

A consideration of mechanisms is not involved in the derivation of the Kd concept in the above generalized manner. Removal onto the solid medium can be due to a number of mechanisms. However, it should be remembered that the trace ion was considered to be in an ideal dilute solution both in the solution and on the soil. The trace ion could conceivably be considered in an ideal dilute solution if it is exchanged onto the soil and occupies only a very small fraction of the soil ion exchange capacity. The requirements that the Kd value remain constant over a concentration range and that the soil-trace ion behave ideally are not compatible with precipitation in solution as a trace ion removal mechanism. With precipitation as a removal mechanism during Kd determinations, the soil becomes an inert system constituent except insomuch as it may affect the system pH and redox environment.

The soil can be considered a passive and incidental part of the removal process unless the trace ion can be shown experimentally to be adsorbed on the solid medium. This can be accomplished by "blank" experiments in which the solution containing the tracer and no soil or rock solids is shaken along with the same solution containing the soil or rock solids. If there is evidence for trace radionuclide removal without the presence of soil or rock solids in the system, the Kd concept is not applicable.

Other practical requirements of a Kd experiment include attainment of equilibrium between the solid medium adsorbed trace ion and the trace ion contained in the solution. Prior to contact of the solid medium and trace ion, the solid medium should be in equilibrium with the none-trace solution macroions. This procedure should be followed to ensure that only the trace ion is adsorbed, and that only in trace concentrations. Trace concentration is shown experimentally by demonstrating that Kd values remain constant over successive trace ion dilutions. This procedure also demonstrates that equilibrium was attained using several solution-solid contact times. The Kd value should refer to a single ionic species, not a mixture of fission products. The basic concept does not allow more than one ionic species to have a constant distribution between two immiscible media.

The Kd is an experimentally derived value that is associated with the circumstances of its determination. It cannot be extended to another chemical system with the same solid exchange medium. Likewise, the Kd from one exchange medium in a given chemical system cannot be used for another solid exchange medium in the same chemical system.

An obstacle to Kd comparisons is the common failure to adequately characterize the solid exchange medium. Even with comparable solution compositions and derived Kd values, the solid exchange materials can be completely different mineralogically, physically and chemically. A bulk chemical analysis, at least a semiquantitative mineralogical and particle size analysis should be performed. Very little of the literature Kd data include such characterizations of the solid phase. With rocks, the characterization work also is very important. Adsorption of radionuclides on rock fissures often is higher than on fresh surfaces because the fissure surfaces have been altered by earlier percolating solutions to minerals such as zeolites or clays that are radionuclide selective and do not occur on fresh rock surfaces. Rancon (1972) suggested calculating Kd based upon surface area rather than the mass of the solid in order to study radionuclide adsorption by impermeable materials such as rocks. This Kd is defined as:

$$\mathrm{Kd(s)} = \frac{\text{surface concentration}}{\text{residual concentration in solution}} \cdot \frac{\text{ml solution}}{\text{cm}^2 \text{ of surface area}} .$$

Using a rock with a known surface area allows better comparisons than a known weight because ion exchange is a surface area function for impermeable rocks. However, once again, good characterization of the rock is required to allow comparisons between rock types, or even within rock types.

The radionuclides which can be expected to react with rocks and soils in other ways than ion exchange include americium, cerium, curium, europium, promethium, plutonium, tritium and zirconium, and sometimes antimony, uranium and ruthenium. Special care should be taken with the above radionuclides to assure that the Kd values obtained are from trace concentrations and that the trace ion is adsorbed on the solid medium. Where the oxidation potential (Eh) is important, such as in plutonium systems, means will have to be found for Kd value determinations in controlled Eh-pH environments.

Many techniques are used or under study for the determination of Kd values including batch tests, low pressure column loading, axial filtration and channel chromatography. The last two techniques are in a development and proving stage, and may or may not be comparable to Kd values determined by a batch technique. The standard Kd determination technique to which all other technique results are compared is the batch technique. It is theoretically possible to derive column Kd values comparable to batch Kd values. However, difficulties are usually encountered in practice because the soil or rock unique hydrologic properties are superimposed on the radionuclide adsorption effects in the resulting breakthrough curve (Baetsle et al., 1966). Consequently, the breakthrough curve is not symmetrical about the 50% breakthrough point and the Kd value as taken at the 50% point is in error. A batch Kd value is determined by agitating a weighed soil or rock sample with a known volume of chemically-characterized solution until the radionuclide attains an equilibrium between solution and soil or rock. To obtain reproducible and comparable radionuclide distribution coefficients, the following experimental requirements should be followed:

1. mineralogically and physically characterize representative rock or soil and chemically characterize the solution before use in Kd measurements,
2. all rocks should be compared on a surface area rather than a weight basis,
3. dry a weighed sample of soil or rock at 105°C to obtain weight corrections for moisture content,
4. pre-equilibrate the solids with nonradioactive waste constituents and discard solution,
5. add the radionuclide at several concentration levels and equilibrate versus time until no significant changes are observed (precipitation of solid phases should be absent),
6. use triplicate samples for each equilibration,
7. a blank solution (containing no soil or rock) should be run along with the samples at each radionuclide concentration level,
8. the equilibrium solution composition should be determined including major cations, anions and organics,
9. the pH should be measured before and after equilibrium, and
10. a controlled redox potential is necessary where it has an effect on the radionuclide oxidation state to assure that only one species of radionuclide is present in the equilibrating solution.

Kd Relationship to Migration

The importance of an accurately determined Kd value cannot be overemphasized when it is used in calculating the velocity of radionuclide movement in geologic materials. If K is equal to the groundwater velocity divided by the radionuclide migration velocity, then $K = 1 + \frac{Kd\ \rho}{\varepsilon}$, where:

Kd = the distribution coefficient = (concentration of radionuclide on the solid/weight of solid)/(concentration in the solution/solution volume in the ml),

ρ = bulk density of medium = weight of solid/volume of solid, and

ε = void fraction = groundwater volume/volume of solid (Burkholder and Cloninger, 1977; Hiester and Vermeulen, 1953; Jackson et al., in press). It may be seen that as the Kd value increases, the radionuclide migration velocity must decrease a proportional amount, if the bulk density of the medium, the void fraction and groundwater velocity are assumed to be constant.

A doubling of the Kd value halves the radionuclide migration velocity in relation to the groundwater velocity. Lester et al. (1975) with their computer model of radionuclide migration have shown schematically the effect of Kd value on radionuclide discharge rate at the outlet of a soil column for a three-membered decay chain. Impulse release was assumed and decay rates of all three radionuclides were neglected. Differences in Kd values for chain members significantly reduced radionuclide discharge rates in comparison to the case when the Kd values for all three radionuclides were the same, including zero.

Field Determination of Kd Values

Using the above equation, a groundwater velocity in the field can be determined between two wells, or between a disposal site and a river bank spring with the use of tritium for a tracer. Another radionuclide can be added to the groundwater and the travel time over the same distance determined for it. If the bulk density and void fraction of the soil can be determined as well, a field Kd can be derived. Eliason (1967) has used the above method to determine the travel times of groundwater and ^{131}I between a ground disposal site and the Columbia River near Hanford N-Reactor. The travel time for ^{131}I was 1.28 times that of the waste water (79 days travel time for ^{3}H, 101 days travel time for ^{131}I). An ^{131}I Kd value of 0.06 ml/g was estimated by Hajek (1968) from these data. An advantage of this field method of Kd measurement is that a resultant Kd value is obtained for soils and rocks which are seldom homogeneous. The laboratory Kd is useful for field applications only if the field soil or rock are assumed to be homogeneous and represented by the laboratory soil sample. However, the laboratory Kd measurement is relatively rapidly accomplished and is inexpensive. The field Kd measurement has the disadvantage of being time-consuming and expensive. Another disadvantage of the field Kd measurements is the difficulty of accurately determining a composite void fraction and bulk density for the field soil, sediment or rock.

An additional method of determining a Kd value for a waste disposal site in the field involves a knowledge of the volume of waste disposal to the ground, the radionuclide concentration per unit volume, the volume and bulk density of the soil and the average radionuclide concentration per unit weight of soil. Essentially this field method is a much larger version of a laboratory Kd determination. A major problem with this type of field Kd determination is that the saturated flow directly beneath the disposal site soon grades into unsaturated flow, with much lower volumes of waste transmitted through the unsaturated flow area. Usually an arbitrary decision is required to select a wetted zone for the average soil radionuclide loading value. An exception would be a radionuclide that is adsorbed very close to the disposal site. Thus, the radionuclides with high Kd values present the least problems with this type of field Kd determination.

An example of the latter type of field Kd is given by Schmalz (1972) who obtained auger samples down to 53 cm in TRA disposal pond bottom sediments at INEL, Idaho. These samples were analyzed for ^{137}Cs, ^{90}Sr, ^{60}Co and ^{144}Ce in three intervals of 0 to 15.3 cm, 15.3 to 30.5 cm, and 30.5 to 45.9 cm. The analytical results were used to estimate the quantities of each of the above radionuclides in the three measured zones and these gradations extrapolated to 15.3 m to obtain a total radionuclide concentration in that volume of sediments. Knowing the volume of sediment and its estimated average bulk density, the radionuclide contents of the sediments, and the volume and radionuclide content of the waste disposed to the TRA pond, Kd values were estimated. The laboratory Kd value for ^{137}Cs was 285 ml/g, for example, while the field Kd value was 600 ml/g. Considering the assumptions as to homogeneity of sediments underlying the TRA pond and their ^{137}Cs content, perhaps the field and laboratory Kd values are not as far apart as the numbers would seem to indicate.

One of the problems associated with the second type of field Kd determination is that usually the influent to the waste disposal site is not constant in either composition or volume, and disposal records are often too generalized to determine waste solution compositional and volumetric variations. Redox potentials and final pH values are seldom known and are difficult to measure in field systems. The experimental requirements for a reproducible laboratory Kd value can seldom be followed for a field Kd determination.

REFERENCES

Ames, L. L., Jr. 1959. The Genesis of Carbonate Apatites. Economic Geology. 54:829-841.

Ames, L. L., Jr. 1960. Some Cation Substitutions During the Formation of Phosphorite from Calcite. Economic Geology. 55:354-362.

Ames, L. L., Jr. 1961a. Anion Metasomatic Replacement Reactions. Economic Geology. 56:521-532.

Ames, L. L., Jr. 1961b. Cation Metasomatic Replacement Reactions. Economic Geology. 56:1017-1024.

Ames, L. L., Jr. 1963. Kinetics of a Replacement Reaction. Economic Geology. 58:1229-1236.

Ames, L. L. 1976. Actinide Occurrences in Sediments Following Ground Disposal of Acid Wastes at 216-Z-9. BNWL-2117, pp. 39-71.

Ames, L. L., Jr., J. R. McHenry and J. F. Honstead. 1958. The Removal of Strontium from Wastes by a Calcite-Phosphate Mechanism. A/CONF. 15/P/395.

Amphlett, C. B. 1964. Inorganic Ion Exchangers. Elsevier Publishing Co., New York.

Andelman, J. B., and T. C. Rozzell. 1970. Plutonium in the Water Environment. 1. Characteristics of Aqueous Plutonium. p. 118-137. IN: Radionuclides in the Environment. Adv. in Chem. Ser. No. 93. The Am. Chem. Soc., Washington, D.C.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Baetsle, L., W. F. Maes, J. Souffriau and P. I. Staner. 1966. Migration de Radio-Elements Dans le Sol. EUR 2481.f.

Bartlett, J. B. and A. G. Norman. 1938. Changes in the Lignin of Some Plant Material as a Result of Decomposition. Soil Sci. Soc. Amer. Proc. 3:210-216.

Belot, Y. and C. Gailledreau. 1963. Kinetics of Strontium-90 Retention by a Calcite-Phosphate Extrapolation Assay. IN: Proc. of an Intern. Symp. on the Retention and Migration of Radioactive Ions in Soils. Saclay, France. Oct. 16-18, 1962.

Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Bierschenk, W. H. 1959. Techniques for Estimating the Specific Retention Properties of Hanford Soils. HW-61644 Rev.

Bray, R. H. and E. E. DeTurk. 1939. The Release of POtassium from Nonreplaceable Forms in Illinois Soils. Soil Sci. Soc. Amer. Proc. 3:101-106.

Broadbent, F. E. and G. R. Bradford. 1952. Cation-Exchange Groupings in the Soil Organic Fractions. Soil Science. 74:447-457.

Burkholder, H. C. and M. O. Cloninger. 1977. The Reconcentration Phenomenon of Radionuclide Chain Migration. BNWL-SA-5786.

Burney, G. A. and R. M. Harbour. 1974. Radiochemistry of Neptunium. NAS-NRC Nuclear Sci. Ser. NAS-NS-3060.

Caldwell, O. G. and C. E. Marshall. 1942. A Study of Some Chemical and Physical Properties of the Clay Minerals Nontronite, Attapulgite and Saponite. Missouri Univ. Agr. Expt. Sta. Res. Bull. 354.

Carroll, D. 1960. Ion Exchange in Clays and Other Minerals. Geol. Soc. Amer. Bull. 70:749-780.

Carroll, D. 1970. Rock Weathering. Plenum Press, NY.

Cassel, D. K., M. Th. Van Grenuchten and P. J. Wierenga. 1975. Predicting Anion Movement in Disturbed and Undisturbed Soils. Soil Sci. Soc. Am. Proc. 39(6):1015-1019.

Chatterjee, B. and M. Paul. 1942. Interaction Between Hydrogen Clays and Neutral Salts. Indian Journ. Agr. Sci. 12:113-120.

Cleveland, J. M. 1970. The Chemistry of Plutonium. Gordon and Breach Science Publishers, New York.

Dean, J. A., Editor. 1973. Lange's Handbook of Chemistry. McGraw-Hill, NY. p. 6-30.

Deer, W. A., R. A. Howie and J. Zussman. 1962. Rock-Forming Minerals. Volume 5, Non-Silicates. Longmans, Green, London. pp. 323-338.

de Haan, F. A. M. 1965. The Interaction of Certain Inorganic Anions with Clays and Soils. Agr. Res. Reports No. 655, 167 pp.

de Haan, F. A. M. 1964. The Negative Adsorption of Anions (Anion Exclusion in Systems with Interacting Double Layers. Journ. Phys. Chem. 68:2970.

de Haan, F. A. M. and G. H. Bolt. 1963. Determination of Anion Adsorption by Clays. Soil Sci. Soc. Am. Proc. 27:178.

Denbigh, K. 1971. The Principles of Chemical Equilibrium, 3rd Edition, Cambridge University Press, London, pp. 256-257.

Dickman, S. R. and R. H. Bray. 1941. Replacement of Adsorbed Phosphate from Kaolinite by Fluoride. Soil Science. 52:263-275.

Drew, J. V. (ed). 1967. Selected Papers in Soil Formation and Classification. Soil Science Society of America, Inc. Madison, Wisconsin.

Dutt, G. R., M. J. Shaffer and W. J. Moore. 1972. Computer Simulation Model of Biophysic - Chemical Processes in Soils. Univ. of Arizona, Tucson. Agric. Exp. Stn. Tech. Bull. 196.

Eliason, J. R. 1967. Field Evaluation of Ground Disposal of Reactor Effluent - 1301-N Crib. BNWL-CC-1032.

Frysinger, G. R. 1960. Cation Exchange Behavior of Vermiculite-Biotite Mixtures. Clays and Clay Minerals. 9:116-121.

Fukai, R. and C. N. Murray. 1974. Adsorption and Desorption of Plutonium and Americium in Freshwater - Sediment and Seawater - Sediment Systems. IN: Activities of the International Laboratory of Marine Radioactivity. IAEA-163, pp. 96-103.

Gaines, G. L. and H. C. Thomas. 1953. Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption. Journ. Chem. Phys. 21:714-718.

Garrels, R. M. and C. L. Christ. 1965. Solutions, Minerals and Equilibria. Harper and Row. New York. pp. 213-216.

Gerasimov, I. P. and M. A. Glazovskaya. 1960. Fundamentals of Soil Science and Soil Geography. Israel Program for Scientific Translations, Jerusalem.

Grebenshchikova, V. I. and Y. P. Davydov. 1961. A Study of the State of Pu(IV) in Dilute Solutions of Nitric Acid. Radiokhimiya. 3:155-164.

Hajek, B. F. 1965. Some Adsorption, Diffusion, and Dispersion Characteristics of Anions in Soils. BNWL-36, pp. 4.1-4.4.

Hajek, B. F. 1966. Plutonium and Americium Mobility in Soils. BNWL-CC-925.

Hajek, B. F. 1968. Waste Disposal to the Ground at 100-N. BNWL-CC-1670.

Hakonson, T. E., J. W. Nyhan and W. D. Purtymum. 1975. Accumulation and Transport of Soil Plutonium in Liquid Waste Discharge Areas at Los Alamos. IAEA-SM-199/99.

Haney, W. A. 1957. Disposal of High Cobalt-60 Scavenged Wastes. HW-48862.

Harmon, C. G. and F. Fraulini. 1940. Properties of Kaolinite as a Function of Its Particle Size. Jour. Amer. Ceram. Soc. 23:252-258.

Harned, H. S. and B. B. Owen. 1958. The Physical Chemistry of Electrolytic Solutions. Reinhold Publishing Corp., NY.

Hiester, N. K. and T. Vermeulen. 1953. Saturation Performance of Ion-Exchange and Adsorption Columns. Chem. Eng. Prog. 48:505-516.

Hillel, D. 1971. Soil and Water. Physical Principles and Processes. Academic Press, New York.

Hofmann, U., A. Weiss, G. Koch, A. Mehler and A. Scholz. 1956. Intracrystalline Swelling, Cation Exchange and Anion Exchange of Minerals of the Montmorillonite Group and of Kaolinite. Natl. Acad. Sci. Publ. 456. pp. 273-287.

Jackson, R. E., W. F. Merritt, D. R. Champs, J. Gulens and K. J. Inch. In Press. The Distribution Coefficient as a Geochemical Measure of the Mobility of Contaminants in a Ground Water Flow System. Paper given at a Conference on the Use of Nuclear Techniques in Water Pollution Studies, 6-9 December 1976, Cracow, Poland, under IAEA Sponsorship.

Jost, W. 1960. Diffusion in Solids, Liquids and Gases. 3rd Edition. Academic Press, New York, NY.

Jurinak, J. J. and J. Santillan - Medrano. 1974. The Chemistry and Transport of Lead and Cadmium in Soils. Utah State Univ., Logan Agric. Exp. Stn. Res. Rep. 18.

Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie/GmbH.

Kelley, W. P. and H. Jenny. 1936. The Relation of Crystal Structure to Base-Exchange and Its Bearing on Base-Exchange in Soils. Soil Science. 41:367-382.

Knoll, K. C. 1960. Adsorption of Strontium by Soils Under Saturated and Unsaturated Flow Conditions. HW-67830.

Latimer, W. M. 1952. Oxidation Potentials. Second Edition. Prentice-Hall, Englewood Cliffs, NJ.

Lester, D. H., G. Jansen and H. C. Burkholder. 1975. Migration of Radionuclide Chains Through an Adsorbing Medium. IN: Adsorption and Ion Exchange. AIChE symposium Series. 71:202-213.

Lindenbaum, A. and W. Westfall. 1965. Colloidal Properties of Plutonium. Int. J. Applied Radiat. Isotop. 16:545.

Lindsay, W. L. 1972. Inorganic Phase Equilibria of Micronutrients in Soils. IN: Micronutrients in Agriculture, pp. 41-57. Soil Sci. Soc. Amer. Inc. Madison, WI.

Mattson, S. 1931. The Laws of Soil Colloidal Behavior. IV. Amphoteric Behavior. Soil Science. 32:343-365.

McAuliffe, C. D., M. S. Hall, L. A. Dean, and S. B. Hendricks. 1947. Exchange Reactions Between Phosphates and Soils. Soil Sci. Soc. Amer. Proc. 12:119-123.

Meinzer, O. E. 1933. Outline of Ground-Water Hydrology with Definitions. U.S.G.S. Water Supply Paper 494.

Mukherjee, J. N., B. Chatterjee, and P. C. Goswami. 1942. Limiting Exchange of Aluminum Ions from Hydrogen Clays on the Addition of Neutral Salts. Jour. Indian Chem. Soc. 19:400-407.

Nelson, J. L., W. A. Haney, K. C. Knoll and D. W. Bensen. 1962. Laboratory Pilot and field Scale Studies of Fission Product Migration Rates in Soil. HW-SA-2744.

Nielsen, D. R. and J. W. Biggar. 1961. Miscible Displacement in Soils: I. Experimental Information. Soil Sci. Soc. Amer. Proc. 25:1-5.

Nielsen, D. R. and J. W. Biggar. 1962a. Miscible Displacement: II. Behavior of Tracers. Soil Sci. Soc. Amer. Proc. 26:125-128.

Nielsen, D. R. and J. W. Biggar. 1962b. Miscible Displacement: III. Theoretical Considerations. Soil Sci. Soc. Amer. Proc. 26:216-221.

Nishita, H., B. W. Kowalesky, A. J. Steen, and K. H. Larson. 1956. Fixation and Extractability of Fission Products Contaminating Various Soils and Clays. I. Sr^{90}, Y^{91}, Ru^{106}, Cs^{137} and Ce^{144}. Soil Science. 81:317-326.

Parker, V. B., D. D. Wagman, and W. H. Evans. 1971. Selected Values of Chemical Thermodynamic Properties. Tables for the Alkaline Earth Elements (Elements 92 through 97) in the Standard Order of Arrangement. NBS Technical Note 270-6.

Posner, A. M. 1966. The Humic Acid Extracted by Various Reagents from a Soil. Part 1. Yield, Inorganic Components and Titration Curves. Jour. Soil Sci. 17:65-78.

Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, England.

Price, S. A. and L. L. Ames. 1975. Characterization of Actinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford. ARH-SA-232.

Rai, D. and W. T. Franklin. 1973. Program for Computing Equilibrium Composition of $CaCO_3$ and $CaSO_4$ Systems from Irrigation Water Compositions. Council of U.S. Univ. for Soil and Water Develop. in Arid and Sub-Humid Areas. Water Manage. Tech. Rep. 29. Colo. State Univ., Fort Collins.

Rai, D. and W. L. Lindsay. 1975. A Thermodynamic Model for Predicting the Formation, Stability and Weathering of Common Soil Minerals. Soil Sci. Soc. Amer. Proc. 39:991-996.

Rai, D. and R. J. Serne. 1977. Plutonium Activities in Soil Solutions and the Stability and Formation of Selected Plutonium Minerals. J. Environ. Qual., 6:89-95.

Rai, D. and R. J. Serne. 1978. Predicted Solid Phases and Solution Species of Elements Generally Present in Radioactive Wastes. DOE Sponsored Document for the National Waste Terminal Storage Program, in publication.

Rancon, D. 1969. Contamination des Sols. Evolution de L'humidite Dans les Sols Non Satures Apres Rejet Sur Une Surface Limitee. CEA-R-3635(1).

Rancon, D. 1972. Practical Utilization of the Distribution Coefficient for the Measurement of the Radioactive Contamination of Minerals in Rocks, Soil and Subterranean Water. ANL-TRANS-931.

Rancon, D. 1973. Contamination des Sols. Comportement des Ions Radioactifs Dans les Sols Non Satures Apres Rejets Dreau Sur Une Surface Limitee. CEA-R-3635(2).

Rancon, D. 1973. The Behavior in Underground Environments of Uranium and Thorium Discharged by the Nuclear Industry. IN: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/55, pp. 333-346 (in French).

Relyea, J. F. 1977. The Behavior of Plutonium in Soil. Ph.D. Thesis. University of Arkansas, Fayetteville, AR.

Rhodes, D. W. 1957a. The Adsorption of Plutonium by Soil. Soil Science. 84:465-471.

Rhodes, D. W. 1957b. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Sci. Soc. Amer. Proc. 21:389-392.

Rossini, F. D., D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe. 1952. Selected Values of Chemical Thermodynamic Properties. NBS Circular 500, Washington, D.C.

Routson, R. C. 1973. A Review of Studies on Soil-Waste Relationships on the Hanford Reservation from 1944 to 1967. BNWL-1464.

Routson, R. C. and R. J. Serne. 1972. Experimental Support Studies for the PERCOL and Transport Models. BNWL-1719.

Samuelson, O. 1963. Ion Exchange Separations in Analytical Chemistry. John Wiley and Sons, NY. pp. 97-112.

Scheffler, K., U. Riege, K. Louwrier, Hj. Matzke, I. Ray and H. Thiele. 1977. Long Term Leaching of Silicate Systems: Testing Procedure, Actinides Behavior and Mechanism. KFK 2456. EUR 5509e.

Schmalz, B. L. 1972. Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station. IDO-10049.

Schofield, R. K. 1947. Calculation of Surface Areas from Measurement of Negative Adsorption. Nature 160:408.

Schnitzer, M. and S. I. M. Skinner. 1965. Organo-Metallic Interactions in Soils: 4. Carboxyl and Hydroxyl Groups in Organic Matter and Metal Retention. Soil Science. 99:273-284.

Schwille, F., W. Lippok and D. Weisflog. 1967. Model Experiments on Fluid Flow in the Transition Zone from Unsaturated to Saturated Soil. IAEA-SM-93/11, pp. 151-159.

Scott, H. D., R. E. Phillips and R. F. Paetzold. 1974. Diffusion of Herbicides in the Adsorbed Phase. Soil. Sci. Soc. Am. Proc. 38:558-562.

Schumm, R. H., D. D. Wagman, S. M. Bailey, W. H. Evans, and V. B. Parker. 1973. Selected Values of Chemical Thermodynamic Properties. Tables for the Lanthanide (Rare Earth) Elements (Elements 62 through 76) in the Standard Order of Arrangement. NBS Technical Note 270-7.

Schwille, F., W. Lippok and D. Weisflog. 1967. Model Experiments on Fluid Flow in the Transition Zone from Unsaturated to Saturated Soil. IAEA-SM-93/11, pp. 151-159.

Sheidina, L. D., and E. N. Kovarskaya. 1970. Colloidal State of Pu(IV) in Aqueous Solutions. Sov. Radio Chem. 12:229-233.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Tamura, T. and D. G. Jacobs. 1960. Structural Implications in Cesium Sorption. Health Physics. 2:391-398.

Tamura, T. and D. G. Jacobs. 1961. Improving Cesium Selectivity of Bentonite by Heat Treatment. Health Physics. 5:149-154.

Tamura, T. 1962. Strontium Reactions with Minerals. TID-7628, pp. 187-197.

Tanji, K. K. and L. D. Doneen. 1966. A Computer Technique for Prediction of $CaCO_3$ Precipitation in HCO_3^- Salt Solution. Soil Sci. Soc. Amer. Proc. 30:53-55.

Thomas, G. W. and A. R. Swoboda. 1970. Anion Exclusion Effects on Chloride Movement in Soils. Soil Sci. 110(3):163-166.

Van Olphen, H. 1963. An Introduction to Clay Colloid Chemistry. Interscience Publishers, New York.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. 1968. Selected Values of Chemical Thermodynamic Properties. Tables for the First Thirty-Four Elements in the Standard Order of Arrangement. NBS Technical Note 270-3.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. 1969. Selected Values of Thermodynamic Properties. Tables for Elements 35 Through 53 in the Standard Order of Arrangement. NBS Technical Note 270-4.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. H. Schumm, and K. L. Churney. 1971. Selected Values of Chemical Thermodynamic Properties. Tables for Elements 54 Through 61 in the Standard Order of Arrangement. NBS Technical Note 270-5.

Winklander, L. 1964. Cation and Anion Exchange Phenomena. IN: Chemistry of Soils, Chap. IV, ACS Monograph. pp. 163-205.

Winograd, I. J. 1974. Radioactive Waste Storage in the Arid Zone. EOS, Trans. Am. Geophys. Union. 55:884-894.

Wood, L. K. and E. E. DeTurk. 1941. The Chemical Effect of Soluble Potassium Salts in Some Illinois Soils. Soil Sci. Soc. Amer. Proc. 5:152-161.

Zadmard, H. 1939. Zur Kenntnis der Kolloidchemischen Eigenschaften des Humus. Kolloid-Beihefte. 49:315-364.

SECTION 3

ELEMENT CHEMISTRY AND GEOCHEMISTRY

The chemistry and geochemistry of the 19 elements chosen for review are examined in the following section from the standpoint of radionuclide migration and retention by geologic materials. Some of the important radioisotopes normally found as fission products or neutron activation products are enumerated. Adequate chemical data were available only for the elements with naturally-occurring stable isotopes. The radiochemistry of all of the isotopes of an element is nearly identical in respect to their reactions with geologic materials, with possible minor exceptions in ^{1}H and ^{3}H. A summary of what is presently known (1977) relative to the radionuclide-geologic media interactions for the selected elements is given. It will be noted that the data presented for cesium and strontium adsorption on soils and rocks are inordinately large. This circumstance is due more to historical accident than to an unusually active experimental interest in cesium and strontium adsorption. In the past, many of the low to intermediate level wastes were disposed to ground. Two of the most hazardous radionuclides contained in these wastes were cesium and strontium, and hence the early interest in examining their migration and retention in soils.

AMERICIUM

Natural Soil and Rock Distributions

The element americium has not been reported to occur naturally in soils or rocks.

Brief Chemistry

Americium has not been reported in nature but is formed in high alpha densities from uranium by the reaction $^{238}U(\alpha,n) \rightarrow {}^{241}Pu \xrightarrow{\beta-} {}^{241}Am$, or from high burnup plutonium having a high ^{241}Pu content by the reaction ^{239}Pu $(n,\gamma) \rightarrow {}^{240}Pu(n,\gamma) \rightarrow {}^{241}Pu \xrightarrow{\beta-} {}^{241}Am$ (Keller, 1971).

The americium radionuclide data of importance to radioactive wastes are given in Table 3-1. It is found in the following four oxidation states: Am(III), Am(IV), Am(V) and Am(VI). The most stable state of americium is the trivalent. The higher oxidation states are strong oxidizing agents and are therefore stable only in media that contain no oxidizable substances (Coleman, 1963). The ionic radius of Am^{+3} is 1.07 Å (Ahrens, 1952).

TABLE 3-1. AMERICIUM RADIONUCLIDE DATA
(KELLER, 1971)

Isotope	Half-Life	Decay Mode
^{241}Am	458 years	α
^{242m}Am	152 years	IT, α
^{242}Am	16 hours	β^-, EC
^{243}Am	7370 years	α

The stability constants and complex formation of Am(III) are probably more well known and studied than any of the other trivalent actinides. The tendency to complex ion formation is a function of factors such as ionic size and charge. In order of decreasing complexing tendency, the actinide series is generally $M^{+4} > MO_2^{+2} > M^{+3} > MO_2^{+}$. For univalent anions, complexing ability with Am(III) follows the order for $F^- > NO_3^- > Cl^- > ClO_4^-$, and for bivalent anions, $CO_3^{-2} >$ oxalate$^{-2} > SO_4^{-2}$ (Keller, 1971).

Solid Phase and Solution Equilibria

Information regarding the possible solid phases of americium in soil and rock environments is lacking. However, the relative solubilities of several americium solids based upon estimated thermodynamic data (Latimer, 1952; Keller, 1971) are given in Figure 3-1 as a function of pH. These are oxides and hydrous oxides of americium contained in an oxidizing environment (pO_2 = 0.68 atm). The solubility of the solids decreases rapidly in the direction of increasing pH. As the environment becomes less oxidizing, the activity of Am^{+3} associated with each of the solid phases [except $Am(OH)_3$] increases rapidly. At $pO_{2(g)} = 8.68$ atm, for example, the curve for Am^{3+} activity from $Am(OH)_4(s)$ increases by two log units.

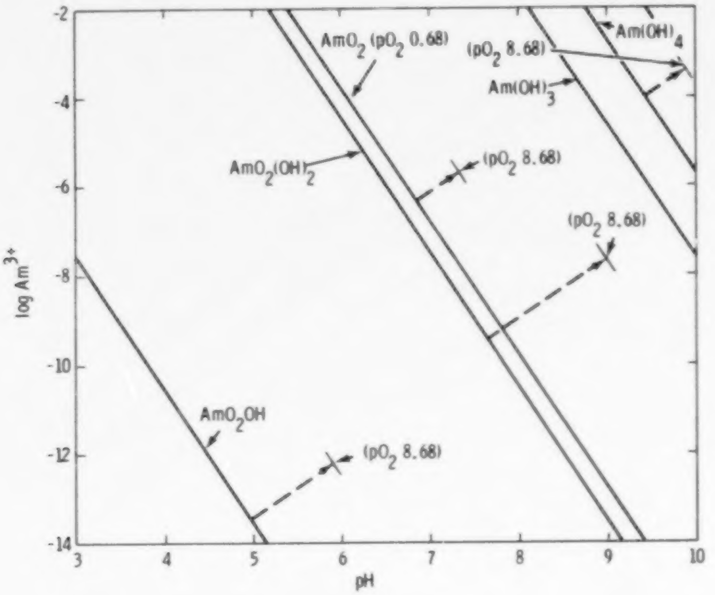

Figure 3-1. The relative stability of various americium solids in an oxidizing soil environment [$pO_{2(g)} = 0.68$ atm]

The activity of various americium species in solution in equilibrium with $AmO_2(s)$ in an oxidizing environment ($pO_2 = 0.68$ atm) is given in Figure 3-2. The thermodynamic data for all the species except $AmOH^{2+}$ and $AmH_2PO_4{}^{2+}$ were selected from Sillen and Martell (1964). The $AmOH^{2+}$ and $AmH_2PO_4{}^{2+}$ data were selected from Keller (1971). In the normal soil pH range, the complex species $Am(OH)^{2+}$ and $AmSO_4{}^{+}$ would control the total activity of americium, with Am^{3+} of somewhat lesser importance. In the environmental conditions chosen, chloride, nitrate and phosphorus species were relatively unimportant in terms of the total americium present in solution. However it should be kept in mind that in a relatively high chloride environment, the $AmCl^{2+}$, for example, could become the principal americium species in solution. With an increase in pO_2 (more reducing environment) and the concentration of anions, the curves given in Figure 3-2 would move upwards. However, the relative position of most of the isotherms would not change. The americium species all of cationic in the normal soil pH range of from 4 to 8. It is to be expected, therefore, that ion exchange could be an important americium removal mechanism.

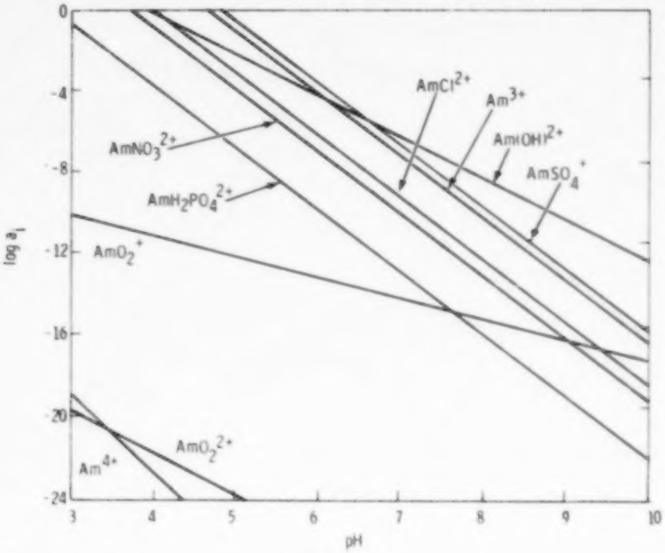

Figure 3-2. The activity of various americium species in equilibrium with $AmO_{2(s)}$ in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm], pSO_4^{2-} = pNO_3^- = pCl^- = 3.0 and $pH_2PO_4^-$ = 5.0.

Experimental Adsorption Results

The adsorption of americium by soils has been studied by several investigators. Hajek and Knoll (1966) and Knoll (1965, 1969) described several americium adsorption experiments on Hanford wastes with emphasis on the effect of organics. An acidic, high salt (5.4M NO_3) waste spiked with organics typically found in waste streams (lard oil, carbon tetrachloride, DBBP and TBP) that contained americium showed very rapid breakthrough when percolated through a Hanford sand. The americium Kd was less than 1 ml/g at a soil-solution pH as high as 3. Plutonium in these solutions had a Kd of

2 to 3 ml/g. If the wastes were neutralized and the resultant supernatant was mixed with 20% by volume organics, the Kd increased to 41 ml/g. A water leach of the neutralized sludge mobilized some americium which, upon contact with soil, yielded an americium Kd of 500 ml/g. In all cases, the americium Kd was less than the plutonium Kd. In other experiments Knoll loaded columns of soil with tap water spiked with americium. Various organic solutions were then percolated through the columns and the quantity of americium leached recorded. One hundred and thirty column volumes of TBP(20%)-CCl_4 (80%) leached 10% of the adsorbed americium versus 5% of the plutonium. DBBP (30%)-CCl_4(70%) after 160 column volumes leached 15% of the americium and 40% of the plutonium. D2EHPA-TBP in normal paraffin hydrocarbons after 30 column volumes leached 80% of the americium and 30% of the plutonium. Hydroxyacetic acid at 0.25M released 100% of the americium and 55% of the plutonium after 10 column volumes. At a lower concentration, 0.025M, hydroxyacetic acid removed 50% of the americium and 40% of the plutonium after 70 column volumes. When the americium and plutonium were added to the organic solution and then percolated through soil columns, the Kd values listed in Table 3-2 were observed, assuming a column bulk density of 1.5 g/ml. There were significant differences between the two cases; americium contacting soil then being leached with organic solutions and americium added directly to organic solutions and contacting soils.

TABLE 3-2. AMERICIUM Kd VALUES FROM SEVERAL ORGANIC SOLUTIONS TBP = TRIBUTYL PHOSPHATE, DBBP = DIBUTYLBUTYLPHOSPHORATE, D2EHPA = Di-(2ETHYLHEXYL) PHOSPHORIC ACID (KNOLL, 1965)

Organic Solution	Americium Kd, ml/g
TBP(20%)-CCl_4(80%)	1.6
DBBP(30%)-CCl_4(70%)	0.6
D2EHPA-TBP in Hydrocarbons	0

Routson et al. (1975) used batch adsorption experiments (10 g soil to 25 ml solution) and 24-hour equilibrations to determine the Kd for americium with desert sand and an Eastern sandy clay. The Kd was determined as a function of solution calcium and sodium concentration at an initial pH of 2.5 to 3.1, and for the sandy clay, decreased as the calcium concentration increased. At 0.002M Ca the americium Kd was 67 ml/g; at 0.20M Ca the Kd was 1 ml/g. For the Burbank sand the Kd was greater than 1200 for all concentrations of calcium. The americium Kd for the sandy clay also was a function of the sodium concentration in solution; 280 at 0.015M Na and 1.6 at 3.00M Na. Although a final pH was not given, the Burbank sand is known to be alkaline, suggesting that americium adsorption may be sensitive to pH.

Van Dalen et al. (1975) determined the americium Kd for Dutch subsoils from 90% saturated NaCl solutions at pH 7 to 8. Samples consisting of mainly illite and kaolinite had a Kd of 5 x 10^4; for a river sand the Kd was 400. Gypsum bearing and clay bearing sandstones had intermediate Kd values. The pH dependence on sorption processes for americium between pH 5-8 was minor.

Fried et al. (1974a, 1974b) determined the adsorption of americium onto a basalt. Addition of salts to the solution lowered the adsorption of americium. La^{+3} and Zr^{+4} cations lowered the americium adsorption much more than Sr^{+2} and Na^{+} suggesting ion exchange as the mechanism controlling adsorption of americium.

In Fried et al. (1977) the distribution of americium at a 32-year-old disposal site in tuff, a very porous, soft volcanic rock, was investigated by coring the tuff at the site to 14 ft. Counting of wafers at different depths down the tuff core showed the americium to be concentrated mainly at a peak at about 9 ft from the disposal site bottom. A core of the same tuff, but uncontaminated, was used to duplicate the field results without much success. A near-surface americium peak was obtained rather than the peak at 9 ft found in the field.

Fried (in press) also studied the movement of ^{241}Am through Los Alamos tuff by using water to elute americium already adsorbed on the tuff. The relative migration ratio for americium was 100 μm/meter of water flow. Upper limit for the relative migration ratio was 500 μm/meter of water flow. Over 95% of the americium was found very close to the point of deposition. Surface adsorption coefficients were derived for americium on National Reactor Testing Station (now INEL) basalt in which the surface area in cm^2 was used rather than the basalt weight in the Kd calculation. In these experiments, rock discs of known surface area were immersed in a solution of 1 x 10^{-7}M $Am(NO_3)_3$.

Small aliquots of the solution were removed and counted at 12-hr intervals until a constant count was reached. The Kd value for americium was 24.4 ± 12 ml/cm^2 for INEL basalt. The values for Kd decreased rapidly as Na^+, Ca^{+2}, Sr^{+2}, La^{+3} and $Zr^{+}4$ ions were added to the americium equilibrating solution in increasing quantities.

Sheppard et al. (1976) reported distribution between 12 characterized soils from various locations and a solution containing $^{241}Am(III)$. The locations included Muscatine, Illinois; Richland, Washington; Barnwell, South Carolina; and Idaho Falls, Idaho. Equilibrations were for up to 4 months with sampling of the solution at intervals. The distribution results are given in Table 3-3. The distribution values ranged from 43,500 ml/g for an Idaho soil to 125 ml/g for a Washington soil. The distribution values were not constant with time, but steadily increased 1% to 86%/month. With Burbank soil, there was a 13% decrease/month. No change was detected for another Washington soil (Hanford). It was postulated that such adsorption behavior was consistent with the Am(III) being in the form of charged colloids or hydrolysis products including Am^{+3}, $Am(OH)^{+2}$, $Am(OH)_2^{\ +}$ and $Am_n(OH)_{2n}^{n+}$ and removal by cation exchange and adsorption. It was reported that the removal of soil organics and raising the system temperature did not appreciably affect the rate of approach to equilibrium or the distribution values. Analysis of the soil cation exchange capacity data indicated a high correlation (r = 0.96) between soil cation exchange capacity and clay content. Correlation does not appear as marked between soil clay content and americium distribution.

Glover et al. (1977) also studied americium sorption by soils. Seventeen characterized soils from around the United States were equilibrated for 48 hr with distilled water solutions containing 10^{-10}M Am and 10^{-8}M Am. Eight replicates were run per soil at each americium concentration. Results were expressed as Kd values. Kd values ranged from 82 to 10,000 on the different soils. Generally, the Kd values for 10^{-10}M and 10^{-8}M Am were the same, or nearly so, with some exceptions. Regression analyses were performed on the americium sorption data to determine whether or not significant relationships existed between americium sorption and soil physical or chemical characteristics. Initial results indicated that a direct relationship existed between soil cation exchange capacity, clay content and americium Kd value.

TABLE 3-3. AMERICIUM 50-DAY DISTRIBUTION. (COMPLETED FROM THE DATA OF SHEPPARD ET AL., 1976)

Soil Identity	Am Distribution, ml/g	Monthly Change in Distribution Ratio
Muscatine silt loam	4,830	+13%
Burbank loamy sand	714	-13%
Ritzville silt loam	971	+1%
Fuquay sand, 0-5 cm depth	476	+32%
Fuquay sand, 5-15 cm depth	417	+32%
Fuquay sand, 15-50 cm depth	249	+27%
Hanford A	125	0%
Hanford B	833	+34%
Idaho A	3,920	+30%
Idaho B	43,500	+86%
Idaho C	37,000	+81%
Idaho D	10,900	+53%

Polzer and Miner (1977) relate americium adsorption data on the same soils to differences in the effective positive charge of americium (Korotkin, 1972) as influenced by system pH. Kd values for americium with several soils from around the United States are given in basic and acidic systems.

Migration Results

Field Studies--

Fowler and Essington (1974) detected a possible difference in solubility between americium and plutonium fallout in soils. Americium may be more soluble than plutonium and may become the radionuclide of prime concern because it has a faster migration rate in soils. Several instances of decreasing Pu/Am ratios with depth in the soil profile could be explained by differential plutonium and americium solubilities.

Laboratory Studies--

Hajek (1966) used contaminated soil samples from the Hanford 216-Z-9 covered trench upper 60 cm to determine the leach rate of americium. Small columns of 5 and 7.5 g of soil were leached with groundwater (composition not given) and 1N $NaNO_3$ at leach rates of less than 4 $ml/cm^2/day$. Effluents were collected at intervals and plotted as percent americium eluted versus column volumes of leaching solution throughput. About 7.5% of the americium was leached with 8 column volumes of groundwater, after which the leach rate became zero. In the other column, about 6.5% of the americium was eluted with 20 column volumes of groundwater, and americium was still being slowly leached. With the 1N $NaNO_3$ leaching, the americium leaching curve level off at 33% americium removed from the column. The author considered this to indicate that at least part of the americium was exchangeable.

Cline (1968) demonstrated that soil pH was directly related to americium migration. Americium nitrate was applied to two soil columns and 254 cm of irrigation applied as an influent. In the acid soil (pH 4.5) the americium was retained in the top 5 cm with 98% in the top 1 cm. Americium penetrated to 20 cm in the basic soil and only 76% remained in the top one centimeter of the column. A larger fraction of the americium was Am^{3+} at 4.5 than at 7.5.

Knoll (1969) studied the problem of disposal of organic wastes to the ground and the affect of this disposal on the adsorption or stripping of radionuclides from the soil column. The organic wastes studied included dibutylbutylphosphonate (DBBP), di-(2-ethylexyl) phosphoric acid (D2EHPA), a mixture of Lard Oil and CCl_4 (Fab Oil), methylisobutylketone (Hexone), a commercial mixture of straight chain hydrocarbons including decane, undecane, dodecane, tridecane and tetradecane (NPS) and tributyl phosphate (TBP). The effect of organics on soil ion exchange properties was studied for an alkaline, Burbank sandy loam soil type by saturating the soil in a 10 cm column with each of the above organics and loading with ^{137}Cs traced water. The cation exchange properties of the soil were not affected by the prior contact with organics, at least in terms of the ^{137}Cs capacity. In other columns, the americium was loaded on the column and then contacted with the organic waste. The americium in the effluent was monitored. The results of leaching with organic wastes is shown in Table 3-4. The soil adsorption of americium carried by organics was investigated by passing the americium-contaminated organics through the same soil. The 50% column breakthrough of americium occurred at 9 column volumes of TBP-CCl_4 (20 to 80%), at 3.5 column volumes of DBBP-CCl_4 (20 to 80%) and the soil adsorbed none of the americium contained in 0.4M D2EHPA-0.2M TBP in NPH.

TABLE 3-4. LEACHING OF AMERICIUM ADSORBED ON THE SOIL BY ORGANIC WASTES (KNOLL, 1969)

Organic Waste	Americium Removal, %	Column Volumes
DBBP-CCl_4 (30 to 70%)	15	80
Fab Oil	1	30
0.4M D2EHPA-0.2M TBP in NPH	80	50
0.25M Hydroxyacetic Acid, pH 3.7	100	5
0.125M Hydroxyacetic Acid, pH 3.8	55	10
0.025M Hydroxyacetic Acid, pH 3.8	50	70

Summary

Americium adsorption (Kd values) on various soils and rocks have been correlated with 1) cation exchange capacity of soils (Sheppard, Kittrick and Hart, 1976; Glover and Miner, 1977), and 2) the concentration of the competing cations (Na^+, Ca^{2+}, Sr^{2+}, La^{3+} and Zr^{4+}) so that the adsorption of americium decreases with an increase in concentration of competing cations (Fried, Friedman and Quarterman, 1974; Fried, Friedman and Weeber, 1974; Routson, Jansen and Robinson, 1975; Sheppard, Kittrick and Hart, 1976; Fried, 1977). Although none of the workers have tried to distinguish the contributions of polymer adsorption, cation exchange, hydrolysis and precipitation to the Kd value, the laboratory data indicate that americium removal from solution may be predominantly via an ion exchange mechanism. This conclusion is supported by the predictions based upon thermodynamic data. The americium species are all cationic in the normal soil pH range from pH 4 to pH 8 (Figure 3-2).

References

Ahrens, L. H. 1952. The Use of Ionization Potentials, Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Cline, J. F. 1968. Uptake of ^{241}Am and ^{239}Pu by Plants. BNWL-714, pp. 8.24-8.25.

Coleman, J. C. 1963. The Kinetics of the Disproportionation of Americium (V). Inorg. Chem. 2:53.

Fowler, E. B. and E. H. Essington. 1974. Soils Element Activities October, 1972 - September, 1973. IN: The Dynamics of Plutonium in Desert Environments. P. B. Dunnaway and M. G. White (eds). NVO-142, pp. 7-16.

Fried, S. (in press) The Retention of Plutonium and Americium by Rock. To appear in Science.

Fried, S., A. M. Friedman, J. Hines, G. Schmitz, and M. Wheeler. 1977. Distribution of Plutonium and Americium at an Old Los Alamos Waste Disposal Site. IN: Proc. Sym. on Dynamics of Transuranics in Terrestrial and Aquatic Environment. Gatlinburg, TN. October 1976.

Fried, S., A. M. Friedman, and L. A. Quarterman. 1974a. Annual Report on Project AN0115A, Fiscal Year 1974. ANL-8115.

Fried, S., A. M. Friedman, and R. Weeber. 1974b. Studies of the Behavior of Plutonium and Americium in the Lithosphere. ANL-8096. pp. 10-11.

Glover, P. A., F. J. Miner, and W. L. Polzer. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. I. Sorption of Plutonium and Americium by Soils. BNWL-2117, pp. 235-246.

Hajek, B. F. 1966. Plutonium and Americium Mobility in Soils. BNWL-CC-925.

Hajek, B. F. and K. C. Knoll. 1966. Disposal Characteristics of Plutonium and Americium in a High Salt Acid Waste. BNWL-CC-649.

Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie/GmbH.

Knoll, K. C. 1965. Reaction of High Salt Aqueous Plus Organic Waste With Soil. BNWL-CC-313.

Knoll, K. C. 1969. Reactions of Organic Wastes in Soil. BNWL-860.

Korotkin, Yu.S. 1972. Study of Transplutonium Element Hydrolysis. II. Hydrolysis of Americium (III) in the Presence of Ions with Positive and Negative Hydration Energy. JIWR-P-6403.

Latimer, W. M. 1952. Oxidation Potentials. Second Edition. Prentice-Hall, Englewood Cliffs, NJ.

Polzer, W. L. and F. J. Miner. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. II. The Effect of Selected Chemical and Physical Characteristics of Aqueous Plutonium and Americium on Their Sorption by Soils. BNWL-2117.

Routson, R. C., G. Jansen, and A. V. Robinson. 1975. Sorption of ^{99}Tc, ^{237}Np and ^{241}Am on Two Subsoils from Differing Weathering Intensity Areas. BNWL-1889.

Sheppard, J. C., J. A. Kittrick, and T. L. Hart. 1976. Determination of Distribution Ratios and Diffusion Coefficients of Neptunium, Americium, and Curium in Soil-Aquatic Environments. RLO-2221-T-12-2.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Van Dalen, A., F. DeWitte, and J. Wiskstra. 1975. Distribution Coefficients for Some Radionuclides Between Saline Water and Clays, Sandstones and Other Samples from the Dutch Subsoil. Reactor Centrum Nederland. 75-109.

ANTIMONY

Natural Soil and Rock Distributions

The average concentrations of antimony found in igneous and sedimentary rocks are given in Table 3-5. Hawkes (1954) reported on the antimony content of the soils of the Nyeba lead-zinc district of Nigeria. Soils that were 30 to 120 meters from ore bodies contained from 1 to 5 ppm Sb. Ward and Lakin (1954) reported 2.3 to 9.5 ppm Sb in Idaho and North Carolina soils.

Boyle (1965) reported that soils from the Galena Hill area, Yukon, Canada, contained on the average 1.0 ppm Sb. Little is known about the behavior of antimony during rock weathering. Antimony may accumulate in shales by adsorption on clay minerals and hydrous oxides such as Mn and Fe precipitates. Antimony may be concentrated in soils relative to igneous rocks, also as an adsorbate.

TABLE 3-5. ANTIMONY CONCENTRATION IN IGNEOUS AND SEDIMENTARY ROCKS (TUREKIAN AND WEDEPOHL, 1961)

ppm						
Igneous				Sedimentary		
Ultramafic	Basaltic	Granitic	Syenite	Shale	Sandstone	Carbonate
0.1	0.2	0.2	0.1	1.5	0.01	0.2

Brief Chemistry

The stable isotopes of antimony found in nature are ^{121}Sb (57.25%) and ^{123}Sb (42.75%). The radionuclides of interest in waste disposal are given in Table 3-6.

TABLE 3-6. ANTIMONY RADIONUCLIDE DATA (WEAST, 1976)

Isotope	Half-Life	Decay Mode
^{124}Sb	60.3 days	β^-
^{125}Sb	2.7 years	β^-
^{126m}Sb	19 minutes	IT, β^-
^{126}Sb	12.5 days	β^-

Antimony may exist in (-III), (0), (III) and (V) oxidation states, readily losing its 2(s) and 3(p) electrons. Ionic radii are Sb^{-3} 2.45 Å, Sb^{+3} 0.76 Å and Sb^{+5} 0.62 Å (Ahrens, 1952). The important antimony minerals include native antimony (Sb), stibnite (Sb_2S_3), jamesonite ($2PbS \cdot Sb_2S_3$), boulangerite ($5PbS \cdot 2Sb_2S_3$), kermesite (Sb_2S_2O) and senarmontite (Sb_2O_3). Stibnite is the most common antimony mineral.

Antimony, in the form of Sb^{+3}, forms complexes such as $Sb(OH)_2^+$, $Sb(OH)_4^-$, $SbCl_3OH^-$, $SbCl_5^{-2}$ and SbS_3^{-3} (Sillen and Martell, 1964). The existence of simple Sb^{+3} and Sb^{+5} is unlikely. Further, Sb is amphoteric. Sb^{+3}, for example, reacts as $Sb_2O_3 + 3H_2O + 2OH \rightarrow 2Sb(OH)_4^-$ in bases, and in acids, $Sb_2O_3 + H_2O + 2H^+ \rightarrow 2Sb(OH)_2^+$. Sb^{+5} dissolves in strong acids forming complexes such as $SbCl_6^-$, and in strong bases forms complex antimonides such as $Sb(OH)_6^-$ (Latimer, 1952). $SbCl_3$ dissolves in a limited amount of water to give a clear solution which, upon dilution, precipitates insoluble oxochlorides such as SbOCl and $Sb_4O_5Cl_2$ (Cotton and Wilkinson, 1962). Izrael et al. (1969) mentioned that ^{125}Sb was amphoteric, with a solubility minimum at pH 7.0.

Solid Phase and Solution Equilibria

Thermodynamic data for Sb_2O_3 (Sillen and Martell, 1964) and Sb_4O_6, $Sb(OH)_3(s)$, $Sb_2O_4(s)$, Sb_2O_5, Sb_2S_3, $SbCl_3$, and SbF_3 (Wagman et al., 1968) compounds were selected and plotted in Figure 3-3 to determine the relative stability of the antimony solid phases. This figure represents a highly oxidizing environment ($O_2 = 10^{-0.68}$). Under these conditions $SbCl_3$, SbF_3, and Sb_2S_3 are very soluble and therefore are not shown.

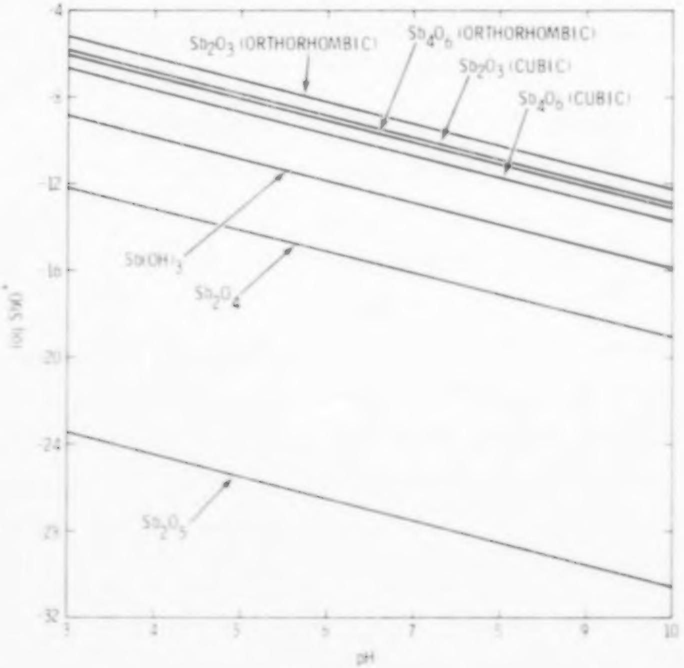

Figure 3-3. The activity of SbO^+ in equilibrium with various antimony solids in an oxidizing soil solution environment $[pO_2(g) = 0.68$ atm].

Under these oxidizing conditions ($O_2 = 10^{0.68}$ atm) the minerals in increasing order of stability throughout the pH range can be arranged as follows: orthorhombic Sb_2O_3, cubic Sb_2O_3, orthorhombic Sb_4O_6, cubic Sb_4O_6, $Sb(OH)_3$, Sb_2O_4, and Sb_2O_5. Solids containing antimony in a +5 state (Sb_2O_5 and Sb_2O_4) and the Sb_2S_3 would change their relative positions with changes in the oxidation-reduction conditions, whereas the other solids will retain their relative positions. Sb_2O_5 and Sb_2O_4 will become less stable with an increase in reducing conditions, while Sb_2S_3 will become the most stable solid phase in extremely reducing conditions. Sb_2S_3 is very soluble in an oxidizing environment because of the oxidation of sulfur to sulfate, which is the stable solution species (Garrels and Christ, 1965). Under extremely reducing conditions and total sulfur levels of approximately 10^{-3}M where the dominant sulfur species is no longer the SO_4^{2-}, the most stable mineral will be Sb_2S_3.

In oxidation-reduction conditions corresponding to oxygen pressures of $<10^{-35}$ atmospheres, $Sb(OH)_3$ would be the most stable solid.

The relative activity of various solution species in equilibrium with $Sb_2O_3(s)$ is given in Figure 3-4. If equilibrium with $Sb(OH)_3(s)$ is assumed, the activity of all the species would be approximately 2.9 log units lower with the lines still parallel to the lines given in Figure 3-4. Thermodynamic data for $Sb(OH)_2^+$ were obtained from Baes and Mesmer (1976) and all the other data were selected from Wagman et al. (1968). In the environmental pH range of interest (4 to 8), it can be seen that $HSbO_2^\circ$ and $Sb(OH)_3^\circ$ are the species that would govern the total activity of antimony present in solution. The other species [$SbOF^\circ$, $Sb(OH)_2^+$, SbO^+, $Sb(OH)_4^-$ or SbO_2^- and $NH_4SbO_2^\circ$] do not contribute significantly to the total antimony present in the solution and hence can be ignored. Since the predominant solution species [$HSbO_2^\circ$, $Sb(OH)_3^\circ$] are neutral, ion exchange as an antimony adsorption mechanism is not expected to be important.

Experimental Adsorption Results

Essington and Nork (1969) used two different models to predict radioactivity migration through basalt and Rainier Mesa tuffs. Many Kd measurements were made, and a Kd for ^{125}Sb of 1.4 ml/g was used in the modeling work.

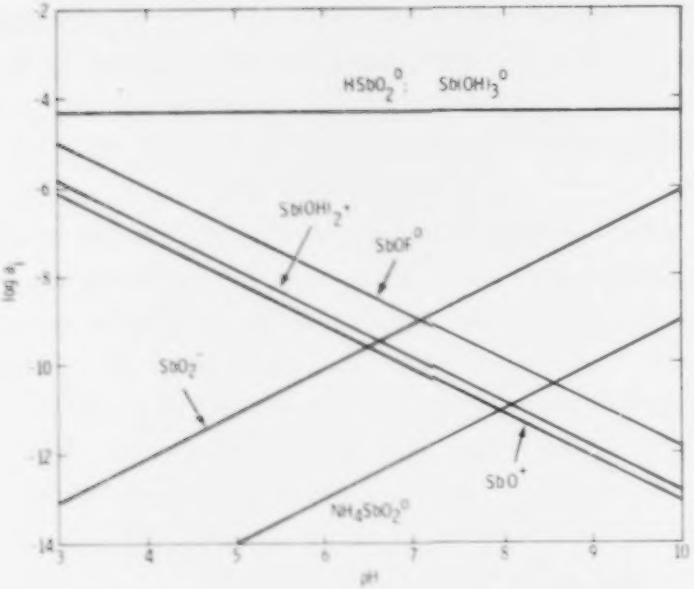

Figure 3-4. The activity of various antimony species in equilibrium with $Sb_2O_{3(s)}$ (cubic) with $pNH_4^+ = 3.0$ and $pF^- = 4.5$. Oxidation-reduction changes do not affect the concentration of species reported in this figure.

^{125}Sb was reported concentrated in Mediterranean bottom sediments by Giacoletto and Triulzi (1970), and ^{124}Sb was suspected by Osterberg et al. (1966) to be present in precipitates collected from treated Columbia River water. ^{124}Sb is not a fission product, but an activation product resulting from the former operation of once-through cooling of the Hanford reactors.

Izrael and Rovinskii (1970) measured the chemical states of fission products in crater water and reported the ^{125}Sb was 85% anionic, 8.5% cationic and 6.5% colloidal. Arnold and Crouse (1971) have determined the radioactive contamination of copper recovered from ore fractured with nuclear explosives. Recovery was simulated by leaching test shot rubble of the radionuclide content given in Table 3-7. One-hundred gram rubble samples were leached for 6 days with 200 ml of synthetic copper ore leach liquor (2g Cu^{+2}, 1g Fe^{+3}, 3g Fe^{+2}/liter as sulfates, with H_2SO_4 to maintain desired pH of 1.0, 2.0 and 3.6). The ^{125}Sb leached from the rubble was about 12% at pH 1.0, 4% at pH 2.0 and too low to permit radionanalysis at pH 3.6. The gross composition of the rubble has not been identified.

TABLE 3-7. RADIOCHEMICAL ANALYSIS OF TEST SHOT DEBRIS SAMPLED ABOUT 200-FT ABOVE THE SHOT POINT AT ABOUT 2 YEARS IN AGE (ARNOLD AND CROUSE, 1971)

Radionuclide	Concentration, dpm/g x 10^4
^{137}Cs	2.1
^{144}Ce	<0.03
^{90}Sr	0.2
^{106}Ru	1.4
^{60}Co	Absent
Gross Gamma	1.0

Adsorption of radionuclides, including ^{125}Sb, by low-grade copper ore in Safford, Arizona, was also determined. The chemical analysis of this ore is given in Table 3-8.

TABLE 3-8. COMPOSITION OF SAFFORD COPPER ORE (ARNOLD AND CROUSE, 1971)

Element	Concentration, wt%	Element	Concentration, wt%
Cu	1.27	Ti	0.66
Al	7.31	K	4.03
Ca	0.006	Na	1.98
Mg	0.73	F	0.10
Fe	3.71	CO_3	0.28
Mn	0.002	ΣS	0.62
Ni	0.011	SiO_2	58.5

Five ml of copper ore leach liquor, of the same composition as listed above, were adjusted in pH with H_2SO_4 and the ^{125}Sb added. The solution was contacted 16 hr with 1 g of minus 20 mesh Safford ore. At pH 1.5, the distribution coefficient obtained was about 40 ml/g, at pH 2.1, about 50 ml/g and at pH 2.7, about 45 ml/g. Arnold and Crouse (1971) state, however, that with other adsorption tests on Safford ore, and with solutions containing ^{125}Sb prepared by leaching radioactive debris, antimony was not as strongly adsorbed as in the above test. These results suggest that the chemical forms of antimony in the two tests were not the same.

R. J. Serne of Battelle, Pacific Northwest Laboratories (PNL), 1973, equilibrated several sediments with simulated neutralized high-level waste solutions containing ^{125}Sb. The sediments and solutions are described in Tables 3-9 and 3-10 and equilibrium distribution values (Kd's) are given in Table 3-11. Some $Ca(OH)_2$ sludge developed in solutions III and IV during makeup. This occurred because of the relatively high calcium nitrate content and final pH (12.0). This sludge was removed before the ^{125}Sb was added, and the solutions were used for Kd measurements. ^{125}Sb levels were measured immediately before use in the Kd measurements so that sludge removal did not affect Kd values.

TABLE 3-9. SOLUTIONS USED IN ^{125}Sb EQUILIBRATIONS WITH GLACIOFLUVIATILE SEDIMENTS FROM WELLS. SEDIMENTS WERE PRE-EQUILIBRATED WITH THESE SOLUTIONS MINUS THE ^{125}Sb ADDED LATER AS A MICROCONSTITUENT

Molarity	Constituent	Solution
1.0	$NaNO_3$	I
0.002	$Ca(NO_3)_2$	
0.65	NH_4NO_3	
0.025	KNO_3	
	pH=12	
4.0	$NaNO_3$	II
0.002	$Ca(NO_3)_2$	
0.65	NH_4NO_3	
0.025	KNO_3	
	pH=12	
1.0	$NaNO_3$	III
3.5	$Ca(NO_3)_2$	
0.65	NH_4NO_3	
0.025	KNO_3	
	pH=12	
4.0	$NaNO_3$	IV
3.5	$Ca(NO_3)_2$	
0.65	NH_4NO_3	
0.025	KNO_3	
	pH=12	
2.6	$NaNO_3$	V
1.18	$NaNO_2$	
0.79	Na_2CO_3	
0.002	$Ca(NO_3)_2$	
0.15	NH_4NO_3	
0.25	$(NH_4)_2SO_4$	
0.01	KNO_3	
	pH=12	

TABLE 3-10. SEDIMENTS USED IN OBTAINING EQUILIBRIUM DISTRIBUTION COEFFICIENTS WITH ^{125}Sb AND THE SOLUTIONS GIVEN IN TABLE 3-9. CAPACITIES WERE DETERMINED ON SEDIMENTS MINUS THE >2mm MATERIALS

Sediment	wt% >2mm Removed	Cation Exchange Capacity, meq/100g	$CaCO_3$ g/100g Sediment
1, silt	0.0	6.96	13.2
2, gravelly sand	39.1	6.73	1.24
3, sand	20.1	6.16	1.30
4, silty sand	5.0	5.95	2.60
5, caliche	--	7.88	37.00
6, silty sand	5.6	5.28	7.65
7, gravel	58.9	6.73	0.95

TABLE 3-11. EQUILIBRIUM DISTRIBUTION COEFFICIENT VALUES (ml/g) BETWEEN SEVEN GLACIOFLUVIATILE SEDIMENTS AND THE SOLUTIONS OF TABLE 3-9 CONTAINING ^{125}Sb. EACH VALUE IS AN AVERAGE OF THREE EQUILIBRATIONS

	Solution				
Sediments	I	II	III	IV	V
1	0.036	0.548	79.7	122.8	0.081
2	0.0	0.483	81.4	71.1	0.045
3	0.0	0.491	55.4	109.0	0.055
4	1.27	2.09	83.7	43.6	0.228
5	0.73	0.56	15.8	14.7	0.140
6	0.65	0.40	15.3	24.1	0.140
7	1.28	1.19	17.6	24.0	0.180

The relatively large ^{125}Sb Kd values obtained on the sediments with solutions III and IV are generally up to three orders of magnitude higher than the Kd values measured with the other solutions. The high calcium solutions also are solutions III and IV, suggesting that precipitation of calcite has scavenged or coprecipitated a portion of the antimony. The solutions were all quite basic in pH(12), enabling them to absorb CO_2 from the air and precipitate $CaCO_3$.

Movement of ^{125}Sb from trenches and seepage pits in the Melton and Bethel Valleys, Oak Ridge, Tennessee, to White Oak Creek was investigated by Duguid (1975, 1976). Typical results are given in Table 3-12. Relatively minor amounts of the ^{125}Sb are found in the groundwater or seepage water compared to the amounts located on the soil. Similar ^{125}Sb values for burial ground 4 in Melton Valley showed a range of from 1.0 to 1.3×10^{-2} dpm/ml in the groundwater and seepage water. This also represents a relatively minor antimony movement from the soil into the groundwater. Computed antimony Kd values ranged from 10^3 to 10^6 ml/g.

TABLE 3-12. ^{125}Sb ANALYSES OF WATER AND SOIL SAMPLES FROM A SEEP NEAR TRENCH 7 (DUGUID, 1976)

Water Samples

Sample Date	Count Rate, dpm/ml
3-5-73	≤ 2.0
3-19-73	≤ 4.0
5-11-73	6.7

Soil Samples

Depth	Count Rate, dpm/g
0-3	≤ 690
3-6	≤ 240
6-9	≤ 120
9-12	≤ 41
12-15	≤ 18
15-18	≤ 13
18-21	≤ 9.7

Several equilibrium adsorption experiments between a radioactive meltglass, a low-grade copper ore and a copper leaching solution were conducted by Jackson (1976) under studies for the nuclear chemical mining of copper. The radionuclides that could be measured in the meltglass included ^{144}Ce,

^{152}Eu, ^{154}Eu and ^{155}Eu. Tracers added to the system to obtain distribution coefficients included ^{85}Sr, ^{88}Y, ^{103}Ru, ^{124}Sb, ^{134}Cs, ^{141}Ce and ^{152}Eu.

The chemical compositions of the glass and chalcopyrite ore are given in Table 3-13. The ore was mostly composed of quartz and sericite with minor feldspar, chlorite, biotite, calcite, chalcopyrite, pyrite and hematite.

TABLE 3-13. CHEMICAL COMPOSITIONS OF MELT GLASS AND PRIMARY COPPER ORE (JACKSON, 1976)

Constituent	Glass, wt%	Ore, wt%
Cu	-	0.7
Fe	1.5	3.2
S	-	2.2
SiO_2	72.3	66.9
Na_2O	4.3	1.5
K_2O	4.3	2.5
CaO	1.9	0.9
MgO	0.47	0.5
Al_2O_3	16.1	15.5
CO_2	-	0.4
TiO_2	0.33	-
Ba	0.05	-
Sr	0.004	-

The chemical composition of the leaching solution is listed in Table 3-14. Distilled water was used instead of leaching solution in a single experiment.

Autoclaves of 300 ml and 3.785 liters capacity were charged with various combinations of leaching solution or water, ore and glass, and then run for lengths of time varying from 47 days to 256 days. Oxygen flow (4 cm^3/sec) was maintained through the system at a temperature of 363 K (90°C). Except for the first experiment, glass and ore leaching was accomplished separately. Glass

TABLE 3-14. COMPOSITION OF LEACHING SOLUTION INFLUENT (JACKSON, 1976)

Species	Concentration, mg/l	Species	Concentration, mg/l
Cu^{+2}	4000	Zn^{+2}	50
Mg^{+2}	2000	Ni^{+2}	30
K+	900	Na^{+}	20
Al^{+3}	800	Co^{+2}	20
Ca^{+2}	500	SO_4^{-2}	25,000
Mn^{+2}	200	NO_3^-	200
Fe^{+3}	100	Cl^-	20

pH adjusted to 1.7 with H_2SO_4

dissolving rates are listed on a surface area basis. ^{124}Sb distribution was computed as a surface area dependent function (Kds) from the measured Kd values for both the ore and the glass. Antimony was one of the most strongly sorbed elements. The ore phases adsorbed antimony activity much more strongly than leaching glass surfaces. In the experiment using water for leaching, the pH of the solution soon fell as a result of reactions with the sulfides in the ore. The ^{124}Sb Kd increased in all cases with reaction time, suggesting that antimony was being removed by the decomposition products forming in the system, such as gypsum, anhydrite or jarosite. In one case, 53.2% of the original ^{124}Sb was found in the solid products. The jarosite composition was nominally $KFe_3(SO_4)_2(OH)_6$, but varied from this as a function of run temperature and growth location. The enrichment of antimony in ion-rich solids could be expected from the similar occurrence in soils and shales.

Migration Results

Field Studies--

Haney and Linderoth (1959) and Haney (1967) studied the disposition of radionuclides beneath several ground disposal waste facilities at Hanford. For example, ^{125}Sb was detected to a depth of 24.4 m in soil sampling wells drilled beneath the 216-BY covered trenches. These trenches were in service from December 1954 to December 1955 and received 3.4 x 10^7 liters of U-plant, high salt, scavenged waste (total dissolved solids = 350 g/l, chiefly $NaNO_3$; pH = 9.5) whose ^{125}Sb content averaged 2 μCi/ml. ^{125}Sb was the major subsurface soil contaminant from the bottom of the covered trenches to 24.4 m. Soil contamination averaged 1.5 x 10^{-3} μCi/g to 18.3 m and fell off rapidly to 1.5 x 10^{-5} μCi/g at 24.4 m. The 216-BC disposal trenches received 4 x 10^{7} liters (0.9 column volumes) of the same type of waste on a specific retention basis, which relies on long-term storage of the waste in the pore space of the soil column above the water table. Approximately 1740 Ci of ^{125}Sb were discharged to the BC-3 covered trench of the BC facility. The ^{125}Sb soil contamination was 1.8 x 10^{-2} μCi/g at 6.1 m, 4 x 10^{-3} μCi/g at 9.1 m and 10^{-5} μCi/g at 12.2 m. For comparative purposes, the ^{137}Cs and ^{90}Sr soil contamination maxima beneath the BY trenches fell by 5 orders of magnitude in the same vertical distance as the ^{125}Sb maxima fell 2 orders of magnitude. The antimony, present in a larger concentration (2 μCi/ml) than ^{137}Cs or ^{90}Sr (0.5 to 0.005 μCi/ml each), does not adsorb on the soil with nearly the Kd value of cesium or strontium, and travels much further down the soil column as a consequence.

The leakage of 435,000 liters of Hanford high salt, high pH (1M NaOH, 5M $NaNO_3$) high level waste from the 241-T-106 underground waste storage tank in 1973 (Anon., 1973) afforded an opportunity to study the migration of the various radionuclides in this waste through the soil column underlying the tank. A series of wells were drilled to obtain contaminated soil samples for radioanalysis. The results showed that antimony, cobalt and ruthenium moved the most rapidly through the soil column. All of these radionuclides tend to form complex species which are neutral or negatively charged, or hydrolyzed species that also are neutral to negatively charged. In either case, the mobility of the antimony can be expected to be relatively high. The caustic content of this waste type is high enough to solubilize a portion of the soil column (Shade, 1974).

Magno et al. (1970) investigated the fate of the radionuclides from the Nuclear Fuel Services plant in western New York state. The plant lagoon system waters and soils were sampled and analyzed. They estimated from these data that approximately 90% of the ^{125}Sb in the plant effluent passed through the lagoon system and into nearby surface streams. Ninety-eight percent of the ^{125}Sb was described as "dissolved" (in solution), exiting from the last lagoon. The antimony is not, therefore, associated with suspended solids, but is in solution, as Figure 3-4 postulates that it should be.

Laboratory Studies--

Laboratory studies on antimony migration through rocks or soils are lacking. There are studies of ^{125}Sb plant availability due to chelation (Hale and Wallace, 1970; Wallace, 1969) and even the use of ^{121}Sb as a groundwater tracer (Jennings and Schroeder, 1968), but little of primary concern with antimony migration.

Saas and Grauby (1973) studied the transfer mechanisms of ^{124}Sb found in reactor cooling water and other wastes to river, irrigated soil and groundwater. The river water contained organomineral pollution in the form of industrial and municipal sewage wastes that interacted with the ^{124}Sb to form chelates, an exchangeable fraction and hydrosoluble components defined as the totality of the organic and mineral components of a soil that are soluble in water. The percentage of the above hydrosoluble ^{124}Sb fraction was plotted versus depth in cm for an alluvial, calcareous soil column receiving ^{124}Sb in river water. Ten to 30% of the ^{124}Sb was in the hydrosoluble form. The point of this work was demonstrating the interactions between pollutants in the river water and ^{124}Sb that results in increased antimony migration. These pollution interactions with radionuclides should be addressed in nuclear reactor siting studies.

Summary

The principal aspect of antimony chemistry that governs its adsorption reactions with soils and rocks over the pH range 4 to 8 is the prevalence of neutral and complexed species (Figure 3-4). Low Kd values are found in high salt, high pH solutions as well (Serne, 1973), with relatively rapid migration through soils (Haney and Linderoth, 1959; Haney, 1967; Anonymous, 1973) and surface waters (Magno et al., 1970). There are indications that antimony can be precipitated or coprecipitated in solids (Serne, 1973), even at low pH values (Jackson, 1976). In low redox conditions ($O_2 < 10^{-35}$ atmospheres), antimony trihydroxide may precipitate and may be a stable compound that controls antimony concentrations (Figure 3-3). Many of the antimony species associated with organopollutants are water soluble (Saas and Grauby, 1973) and migrate readily with the water. Thermodynamic data on the antimony complexes formed with soil organic materials do not exist at present because the complexes are chemically poorly defined, and in many cases, unknown.

References

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.

Arnold, W. D. and D. J. Crouse. 1971. Radioactive Contamination of Copper Recovered from Ore Fractured with Nuclear Explosions. ORNL-4677.

Baes, C. F. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Boyle, R. W. 1965. Geology, Geochemistry, and Origin of the Lead-Zinc-Silver Deposits of the Keno Hill-Galena Hill Area, Yukon Territory. Geol. Surv. Canada Bulletin III.

Cotton, F. A. and G. Wilkinson. 1962. Advanced Inorganic Chemistry. Interscience Publishers.

Duguid, J. O. 1975. Status Report on Radioactivity Movement from Burial Ground in Melton and Bethel Valleys. ORNL-5017.

Duguid, J. O. 1976. Annual Progress Report of Burial Ground Studies at Oak Ridge National Laboratory. Period Ending September 30, 1975. ORNL-5141.

Essington, E. H. and W. E. Nork. 1969. Radionuclide Contamination Evaluation-Milrow Event. NVO-1229-117.

Garrels, R. M. and C. L. Christ. 1965. Solutions, Minerals and Equilibria. Harper and Row. New York. pp. 213-216.

Giacoletto, C. and C. Triulzi. 1970. Radiochemical Studies for Radioactivity Determinations on Marine Sediment Samples: Cs-137, Sb-125, and Co-60. CISE-N-118.

Hale, V. O. and A. Wallace. 1970. Effect of Chelates on Uptake of Some Heavy Metal Radionuclides from Soil by Bush Beans. Soil Sci. 109:262-263.

Haney, W. A. and C. E. Linderoth. 1959. Exploratory Field Study of a Ground Waste Disposal Facility. HW-60115.

Haney, W. A. 1967. Final Report on the Effects of Ben Franklin Dam. BNWL-412.

Hawkes, H. E. 1954. Geochemical Prospecting Investigations in the Nyeba Lead-Zinc District, Nigeria. U.S.G.S. Bulletin 1000-B.

Izrael, U. A., V. N. Petrov, A. A. Pressman, F. A. Rovinsky, E. D. Stukin, and A. A. Ter-Saakov. 1969. Radioactive Contamination of the Environment by Underground Nuclear Explosions and Methods of Forecasting It.

Izrael, Yu.A. and F. Ya. Rovinskii. 1970. Hydrological Uses of Isotopes Produced in Underground Nuclear Explosions for Peaceful Purposes. UCRL-Trans-10458.

Jackson, D. D. 1976. Radiochemical Studies for the Nuclear Chemical Mining of Copper. UCRL-52025.

Jennings, A. R. and M. C. Schroeder. 1968. Evaluation of Selected Isotopes as Ground Water Tracers. Water Resour. Res. 4:829-838.

Latimer, W. M. 1952. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. Prentice-Hall, Inc.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Osterberg, C., N. Cutshall, V. Johnson, J. Cronin, D. Jennings, and L. Frederick. 1966. Some Non-Biological Aspects of Columbia River Radioactivity. IN: Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters. IAEA-SM-72/18A, pp. 321-335.

Saas, A. and A. Grauby. 1973. Mechanisms for the Transfer to Cultivated Soils of Radionuclides Discharged by Nuclear Power Stations into the System: River-Irrigated Soil--Ground Water. IN: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/57, pp. 255-269.

Shade, J. W. 1974. Reaction of Hanford Sediments with Synthetic Waste, A Reconnaissance Study. ARH-CD-176.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. The Chemical Society.

Turekian, K. K. and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Bull. Geol. Soc. America. 72:175.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halon, S. M. Bailey, and R. H. Schumm. 1968. Selected Volumes of Chemical Thermodynamic Properties. U.S. Department of Commerce.

Wallace, A. 1969. Behavior of Certain Synthetic Chelating Agents in Soil and Biological Systems. UCLA-34-P-51-26, 92 p.

Ward, F. N. and H. W. Lakin. 1954. Determination of Traces of Antimony in Soils and Rocks. Analytical Chemistry. 26:1168-1173.

Weast, R. C., Editor. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio, pp. B301-B302.

CERIUM

Natural Soil and Rock Distributions

The abundance of cerium in rocks is given in Table 3-15. Cerium generally increases in concentration from basaltic to granitic rocks. In a study of Russian platform soils, Balashov et al. (1964) found that the soils with highest cerium contents were alkaline, suggesting precipitation as the hydroxide. The acid soils were lower in cerium because cerium had been removed and had migrated. Soils derived from granitic rocks could be expected to show the highest cerium contents if the weathering resulted in an alkaline environment. Vinogradov (1959) gave the average cerium content of soils as 50 ppm. Half, or more, of the cerium in rocks is found in accessory minerals such as apatite, while the remainder also substitutes for calcium but only in the main stage minerals such as plagioclase.

TABLE 3-15. CERIUM ABUNDANCE IN ROCKS

Rock Type	Ce, ppm	Reference
Continental basalts	59	Frey et al., 1968
Kimberlite	119	Burkov and Podporina, 1966
Ultramafic	0.1	Turekian and Wedepohl, 1961
Basaltic	48	Turekian and Wedepohl, 1961
Granitic, high Ca	81	Turekian and Wedepohl, 1961
Granitic, low Ca	92	Turekian and Wedepohl, 1961
Syenites	160	Turekian and Wedepohl, 1961
Shales	59	Turekian and Wedepohl, 1961
8616 Russian platform shales	67	Ronov et al., 1967
6051 Russian platform sandstones	33	Ronov et al., 1967
11205 Russian platform limestones	6.5	Ronov et al., 1967
average of above	57	Ronov et al., 1967
Sandstones	92	Turekian and Wedepohl, 1961
Dolomite and limestones	11.5	Turekian and Wedepohl, 1961

Brief Chemistry

Cerium occurs naturally in four stable isotopes shown in Table 3-16. The radioisotopes ^{141}Ce and ^{144}Ce are both present in radioactive wastes as fission products with half-lives of 33 days and 284 days, respectively. After 100 years, little fission product cerium remains.

TABLE 3-16. STABLE ISOTOPES OF CERIUM
(INGHRAM ET AL., 1947)

Isotope	Natural Abundance, %
^{136}Ce	0.15
^{138}Ce	0.25
^{140}Ce	88.5
^{142}Ce	11.1

The usual oxidation state of cerium is tripositive with ionic radius of 1.03 Å (Ahrens, 1952).

The solubility product of Ce(III) hydroxide was given by Vickery (1953) as 1.5×10^{-20}. For comparison, the solubility products of $Al(OH)_3$ and $Fe(OH)_3$ are 3.7×10^{-15} and 3.8×10^{-38}, respectively (D'Ans and Lax, 1967).

In geologic environments, cerium forms weak complexes. Cerium complexes of interest to soil environments will be reviewed in a subsequent section. The most important and the most common cerium minerals include monazite (light rare earths, Th) PO_4 and bastnaesite (light rare earths, Th) FCO_3. Many other cerium-containing minerals exist but most are relatively rare.

Solid Phase and Solution Equilibria

The relative stability of various cerium solid phases is shown in Figure 3-5. The thermodynamic data of the compounds used in Figure 3-5 were obtained from Schumm et al. (1973), for Ce_2O_3 and CeO_2, Baes and Mesmer (1976) for $Ce(OH)_3$ and Sillen and Martell (1964) for $CePO_4$. Among the solids depicted in Figure 3-5, CeO_2 is the only one that changes its position with a change in oxidation-reduction conditions. In an oxidizing environment ($pO_2 < 23.68$ atm), the solids in increasing order of stability are Ce_2O_3,

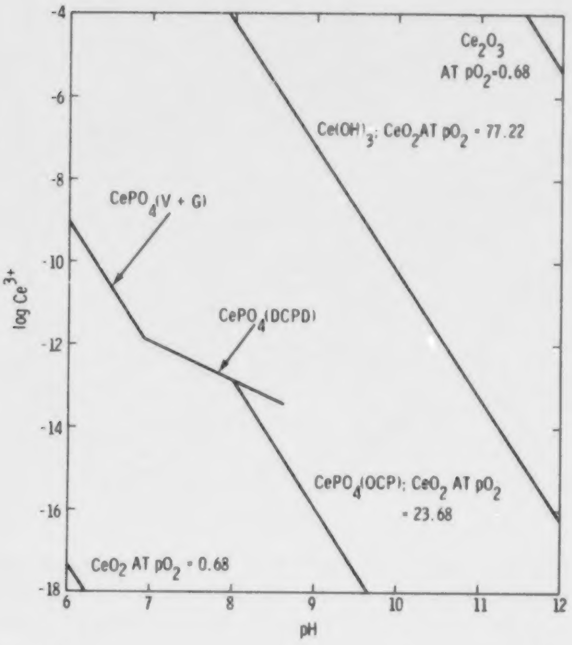

Figure 3-5. The activity of Ce^{3+} in equilibrium with phosphate levels from Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP).

$Ce(OH)_3$, $CePO_4$, and CeO_2. Ce_2S_3 is too soluble to plot in Figure 3-3 in an oxidation-reduction environment where SO_4^{2-} will be the most dominant sulfur species. In oxidation-reduction conditions corresponding to pO_2 of >23.68, $CePO_4$ would be the most stable solid phase.

The activity of various solution species of cerium in equilibrium with $CePO_4$(solid) and under such concentrations of F^-, Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-} as commonly found in the environment is shown in Figure 3-6. The thermodynamic data for all of the hydrolysis species were obtained from Baes and Mesmer (1976). The data for $CeNO_3^{2+}$ were obtained from Sillen and Martell (1964). All the other data were obtained from Shumm et al. (1973). Since Figure 3-6 is based on solution complexes in equilibrium with Ce(III) as $CePO_4$, Ce(IV) ions and complexes would decrease in activity with increase in reducing conditions. In the environmental pH range of interest the Ce(IV) ions and complexes do not contribute significantly to the total cerium concentration in solution.

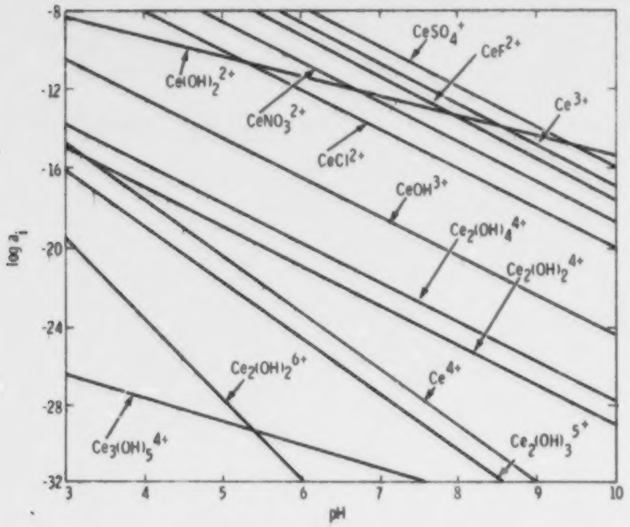

Figure 3-6. The activity of various cerium species in equilibrium with $CePO_{4(s)}$ in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm], $pF^- = 4.5$, $pCl^- = pSO_4^{2-} = 2.5$, $pNO_3^- = 3.0$ and $pH_2PO_4^- = 5.0$.

Trivalent cerium species in increasing order of importance are $CeCl^{2+}$, $CeNO_3^{2+}$, CeF^{2+}, Ce^{3+}, and $CeSO_4^+$. Thus, $CeSO_4^+$ would be the most dominant solution species in the environmental pH range of interest (pH 4 to 8).

Experimental Adsorption Results

Nishita et al. (1956) studied five soils and two clay minerals in systems with ^{144}Ce. Pretreatment of bentonite with dilute acid gave much less cerium uptake by the clay than the untreated bentonite. The hydrogen ion was more strongly adsorbed than ^{144}Ce. The pH of the leaching solution had a profound effect on release of cerium by the soils. At pH values less than 5, 99.5% recoveries of ^{144}Ce were reported.

Rhodes (1957) studied the uptake of ^{144}Ce on a Hanford soil as a function of pH. The Kd values rose steadily from 3.0 at pH 1.6 to >1980 at pH 6.1. The Kd then decreased to a minimum of about 100 at pH 10 and increased again to >1980 at pH 12 and above. The reduced uptake by soil of cerium between pH 7 to 12 did not occur in the presence of macroconcentrations (3M) of sodium ions. Thus, the ^{144}Ce was present either as a radiocolloid in this region, which was flocculated by the high concentration of sodium ions, or as an ion species that was altered by the sodium ions to increase uptake by the soil. The complete removal of 4.2×10^{-2}M cerium at pH 5.5 to 6 was reported, which at this concentration exceeded the capacity of the soil by ten times. The precipitation of cerium hydroxide was indicated.

Bensen (1960) reported that cerium adsorbed on the soil could not be exchanged above pH 7.4 and was difficult to exchange at pH 5.5 to 7.4. The fraction of cerium exchanged by barium at pH 5.5 was 10% and virtually none at pH 7.4. All of the cerium could be removed by ion exchange at pH 2.2, with less removal as a function of pH to 7.4 when none of the cerium was exchangeable from the soil. Above pH 7.0, the presence of 0.5M alkali metal cations and 0.25M alkaline earth metal cations did not affect cerium removal from solution by soil. Below pH 3.0, the adsorption of cerium was depressed similarly by accompanying salts, implying that the cerium is ionic below pH 3.0 and removed by ion exchange on the soil.

Bensen (1960) reported that the soil uptake of cerium added as Ce(III) was identical to that added as Ce(IV). However, when an oxidizing agent ($NaBiO_3$) was added, uptake of Ce(IV) increased to 99% at pH 1, while only 58% of the Ce(III) was adsorbed at this pH. Bensen concluded that the absence of sufficient holding oxidant resulted in an immediate reduction of Ce(IV) to Ce(III) by contact with the soil.

Kokotov et al. (1962) investigated ^{144}Ce adsorption by soils and found that cerium adsorption was much less below pH 2.0 due to increased hydrogen ion competition.

Bochkarev et al. (1964) reported that 85% of ^{144}Ce applied to soil surfaces was accounted for 2 years following the application in the top 5 cm of medium and coarse clay loams.

Kampbell (1964) investigated ^{144}Ce uptake by colloidal suspensions of kaolinite, illite and montmorillonite type clays, all of which had a high affinity for ^{144}Ce. Only under very acid conditions did the cerium remain in solution. DTPA also was effective in keeping cerium in solution at trace levels.

Dlouhy (1967) studied the distribution coefficients of cerium on Casaccia soil and tuff both in the laboratory and in field experiments. The laboratory distribution coefficients ranged from 1050 to 1300 cm^3/g for the cerium on the soil and 3000 to 3800 cm^3/g for cerium on the tuff. The solution conditions and soil and tuff were not characterized. Coring of seepage pits showed the cerium to be essentially contained in the upper 6 cm of the pit soil.

Molchanova (1968) studied the adsorption of ^{144}Ce by soils and found better uptake at acidic pH values above 2.0 than at neutral to alkaline values. Cerium was more easily removed from soils by iron salts than aluminum or copper salts. The presence of iron colloids in the soil reduced the sorption of ^{144}Ce more sharply than did iron salts.

Brown et al. (1969) studied the formation of ^{144}Ce colloids and the adsorption of cerium by humic acid and bentonite suspensions. As ionic strength and cerium concentration decreased and pH increased, equilibrium shifted toward radiocolloidal cerium. At pH 6.5 and ionic strength of 10^{-3}, about 90% of the cerium was in the radiocolloidal form. A multiple regression equation is given that shows the effects of pH, ionic strength and cerium concentration on radiocolloidal cerium in solution.

Migration Results

Field Studies--

Magno et al. (1970) determined the forms and relative mobilities of radionuclides from the lagoon system of the Nuclear Fuel Services plant in Western New York state. They reported that 0.02 Ci of ^{144}Ce were discharged from the last lagoon from May to October 1969. None of the discharged ^{144}Ce activity was dissolved in the water. All of the ^{144}Ce activity discharged was found in the suspended solids. Approximately 8.5 Ci of ^{144}Ce were discharged from the plant to the lagoon system over the same time period (May-October 1969). Thus, although all of the cerium was in particulate form, about 3% migrated through the lagoon system in the form of suspended solids.

The migration of 435,000 liters of liquid high-level waste ($\sim$5M $NaNO_3$, 1M NaOH) from 241-T-106 underground tank through Hanford soils was followed by the drilling of several sample wells after the event (Anon., 1973). The contaminated soil zone was determined on the basis of these analyses and the relative migration distances of the radionuclides evaluated. The rare earths, including cerium, were more mobile than plutonium and cesium but less mobile than antimony, cobalt and ruthenium. Cerium could be expected to be at least partially complexed in such a high salt, high pH solution.

Brookins (1976) reported that the rare earth elements including cerium have been retained at the site of a 1.8 billion year old fossil nuclear reactor at Oklo, Gabon. The rock surrounding the reactor is shale infilling a fracture system in organo-argillaceous sandstone.

Laboratory Studies--

Nishita et al. (1956) studied the extractability of ^{144}Ce from clays and soils with distilled water and 1M ammonium acetate. The fraction remaining on the soil or clay mineral (bentonite and kaolinite) after the acetate elution or leaching solution was passed through the column was called the nonexchangeable ^{144}Ce fraction. For both the soils and clays, ^{144}Ce was hardly moved by the water leaching or exchanged from soils or bentonite. Kaolinite showed a large portion of exchangeable ^{144}Ce and a relatively small amount of nonexchangeable ^{144}Ce. Most of the ^{144}Ce on the soils and on the bentonite were in the nonexchangeable fraction. The somewhat more acid nature of the kaolinite probably accounts for the larger percentage of cerium associated with it as exchangeable cerium.

Schulz (1965) included cerium and the other rare earths under the category of immobile radioactive elements. These elements were precipitated as hydroxides or carbonates or were very strongly bound by soil clays. Perhaps this view should be somewhat tempered by the previous cases of ^{144}Ce migration as a particulate or in complexed species.

Eichholz et al. (1967) studied the fractionation of several radioactive elements between several natural waters and the suspended solids contained in them. The results gave an indication of the ability of cerium to migrate as a suspended solid or adsorbed on the suspended solids already present in most natural waters. The suspended solids are characterized in Table 3-17. The most obvious relationship is a direct one between the suspended solids content and cerium adsorption. However, there also is a

TABLE 3-17. ADSORPTION OF ^{144}Ce ON SUSPENDED SOLIDS (EICHHOLZ ET AL., 1967)

Water Source	^{144}Ce Removed, %	Suspended Solids, mg/l	Dissolved Solids, mg/l	pH
Colorado River	72.0	299	350	7.5
Camp McCoy	44.6	12	60	6.9
Bayou Anacoco	36.9	24	63	6.2
Lodgepole Creek	96.9	965	200	6.8
Chattahoochee River	26.1	131	31	7.3

suggestion of an inverse relationship between cerium adsorption and solution pH. At the lower pH, more of the cerium should be present as cationic species and hence better able to adsorb on the suspended solids. It should also be pointed out that the Lodgepole Creek solids are largely montmorillonite, a high exchange capacity clay mineral.

Summary

No information is available on solid compounds of cerium that may be present in soils and sediments. It appears that $CePO_4$ (Figures 3-5 and 3-6), especially in alkaline conditions, may form in soils and sediments and may control cerium concentrations.

In all terrestrial environments Ce(IV) and its complexes would have insignificant effects on cerium concentration (Figure 3-6). Thus, cerium would be expected to be present as Ce(III) (Figure 3-6 and Ahrens, 1952; Bensen, 1960). In the absence of strong complexing ligands, and especially in acidic environments, cerium would be expected to be present as Ce^{3+} (Figure 3-6; Bensen, 1960) and ion exchangeable. The increase in pH has been shown to increase the cerium adsorption (Rhodes, 1957; Bensen, 1960; Nishita, 1956; Kokotov et al, 1962; Kampbell, 1964). As expected, the presence of complexing ligands such as DTPA increases cerium concentration in solution and reduces adsorption (Kampbell, 1964). In slightly acidic (pH 6.5) to alkaline conditions, cerium is thought to be present as radiocolloid which has been shown to increase adsorption (Rhodes, 1957; Brown et al., 1969). Kampbell (1964) reported that kaolinite, montmorillonite, and illite have a strong affinity for cerium. Cerium adsorbed on suspended solids has been shown to migrate in field and laboratory studies (Magno et al., 1970; Eichholz et al., 1967). However, this type of movement would be expected to be dependent upon the particle size of the suspended solids and the pore size distribution of soils and rocks.

References

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.

Baes, C. F., Jr. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Balashov, Y. A., A. B. Ronov, A. A. Migdisov, and N. V. Turanskaya. 1964. The Effects of Climate and Facies Environments on the Fractionation of the Rare Earths During Sedimentation. Geochemistry International. 10:951-969.

Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Bochkarev, V. M., Z. G. Antropova, and E. I. Belova. 1964. Migration of Strontium-90 and Cerium-144 in Soils of Different Texture. Soviet Soil Science. 9:936-938.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brown, R. E., R. E. Franklin, and R. H. Miller. 1969. Reactions of Cerium-144 in Solution and Suspensions of Soil Humic Acid and Bentonite. Soil Science Society of America, Proceedings. 33:677-681.

Burkov, V. V. and Ye. K. Podporina. 1966. First Data on Rare Earths in Kimberlite. Dokl. Acad. Sci. USSR. Earth Science Section. 171:215-219.

D'Ans, J. and E. Lax. 1967. Taschenbuch für Chemiker and Physiker. 3 Aufl., Bd. I. Springer.

Dlouhy, A. 1967. Movement of Radionuclides in the Aerated Zone. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/18, pp. 241-249.

Eichholz, G. G., T. F. Craft, and A. N. Galli. 1967. Trace Element Fractionation by Suspended Matter in Water. Geochim. et Cosmochim. Acta. 31: 737-745.

Frey, F. A., M. A. Haskin, J. A. Poetz, and L. A. Haskin. 1968. Rare Earth Abundances in Some Basic Rocks. J. Geophys. Res. 73:6085-6098.

Inghram, M. G., R. J. Hayden, and D. C. Hess, Jr. 1947. The Isotopic Constitution of Lanthanum and Cerium. Phys. Rev. 72:967-970.

Kampbell, D. H. 1964. Cerium, Iron, and Manganese Sorption by Soil Colloids and Uptake by Plants. Thesis. Univ. of Missouri.

Kokotov, Yu. A., R. F. Popova, I. Tsing-Chih, and M. Shih-tsi. 1962. Sorption of Long Lived Fission Products by Soils and Argillaceous Minerals. II. Sorption of Cerium-144 by Soils. Radiokhimya. 4:227-228.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Molchanova, I. V. 1968. Behavior of Cerium-144, in Various Types of Soil. Tr. Inst. Ekol. Rast. Zhivotn. 61:4-11.

Nishita, H., B. W. Kowalewsky, A. J. Steen, and K. H. Larson. 1956. Fixation and Extractability of Fission Products Contaminating Various Soils and Clays: I. Strontium-90, Ruthenium-106, Cesium-137, and Cerium-144. Soil Science. 81:317-326.

Rhodes, P. W. 1957. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Science Society of America, Proceedings. 21:389-392.

Ronov, A. B., Yu. A. Balashov, and A. A. Migdisov. 1967. Geochemistry of the Rare Earths in the Sedimentary Cycle. Geochemistry International. 4:1-17.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Schumm, R. H., D. D. Wagman, S. M. Bailey, W. H. Evans, and V. B. Parker. 1973. Selected Values of Chemical Thermodynamic Properties. Tables for the Lanthanide (Rare Earth) Elements (Elements 62 through 76) in the Standard Order of Arrangement. NBS Technical Note 270-7.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Turekian, K. K. and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Bull. Geol. Soc. America. 72:175.

Vickery, R. C. 1953. Chemistry of the Lanthanons. Butterworths Science Publications.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.

CESIUM

Natural Soil and Rock Distribution

The cesium content of several rock types is given in Table 3-18. Bertrand and Bertrand (1949) studied the soils of France and Italy and found the largest concentration of cesium in soils over igneous rocks and in alkaline soils. A range of 0.3 to 25.7 ppm Cs was reported. Approximately 5 ppm Cs was reported by Vinogradov (1959) in soils of the Russian Plains and 1 ppm in Japanese soils. An average of 1.1 ppm Cs was found in suspended material and 2.6 ppm Cs in bottom sediments of seven western United States streams (Sreekumaran et al., 1968). Hirst (1962) studied the cesium content of modern marine sands and clays, and reported them to contain 1.0 to 3.2 ppm Cs and 7.9 to 13 ppm Cs, respectively. In general, cesium is enriched in the potassium minerals, although enrichment may only consist of a few hundred ppm cesium. The large size of the cesium cation makes it difficult for it to substitute in crystal positions normally occupied by potassium, its nearest geochemically abundant, alkali metal relative. Hence, cesium often becomes concentrated enough to form its own mineral phase (pollucite).

TABLE 3-18. CESIUM CONTENT OF ROCKS

Rock Type	Cs Content, ppm	Reference
Basalt (estimated average)	1.1	Turekian and Wedepohl, 1961
Basalt (estimated average)	1.7	Heier and Adams, 1964
Basalt (estimated average)	1.0	Taylor, 1964
Basalt (estimated average)	1.0	Taylor and White, 1966
Granodiorite	3.0	Heier and Adams, 1964
Granite	6.8	Heier and Adams, 1964
Granite	5.0	Taylor, 1964
Granites, Russia	5.5	Beus and Fabrikova, 1961
Marine shales	5.0	Horstman, 1957
Sandstone	1.0	Horstman, 1957
Limestone	1.0	Horstman, 1957
Modern sediments	6.0	Horstman, 1957

Brief Chemistry

The only stable isotope of cesium is ^{133}Cs. Fission product cesium radioisotopes include four main cesium isotopes, with only ^{134}Cs, ^{135}Cs and ^{137}Cs (half-lives of 2.05 years, 3×10^6 years and 30.23 years, respectively) of significant concentrations 10 years after separation from PWR (Pressurized Water Reactor) fuels (Schneider and Platt, 1974). Pollucite, (Cs, Na) $(AlSi_2O_6) \times H_2O$ containing 22 to 36 wt% cesium, is the only independent cesium mineral of any importance.

In all its natural compounds, cesium occurs as a monovalent cation with a radius of 1.67Å (Ahrens, 1952). There is little, if any, tendency for cesium to form complexes in natural environments, and the solubility of most cesium compounds in water is very high.

Solid Phase and Solution Equilibria

Thermodynamic data was collected for the following solid phases of cesium: Cs(OH), Cs_2O, CsCl, $CsClO_4$, Cs_2SO_4, Cs_2CO_3, $CsHCO_3$, $CsNO_3$, CsF. All are highly soluble and, therefore, solid phase diagrams for cesium are not presented.

Baes and Mesmer (1976) report that cesium may be associated with OH^- ions in solution and that the extent of this association cannot be estimated accurately. Charlot (1957) reported that cesium rarely forms solution complexes. Therefore cesium would be expected to appear in solutions predominantly as Cs^+. Only 1.5% of the cesium from underground nuclear explosions was found (Izrael et al., 1970) to be colloidal, which may have been adsorbed on other colloids. The main soil and rock reaction with cesium is expected to be ion exchange.

Experimental Adsorption Results

The effect of cesium concentration and pH on cesium adsorption by a Hanford calcareous soil was studied by McHenry (1954). The data indicated that trace cesium concentrations are essentially completely adsorbed above pH 4.0. When accompanied by 4M NaCl, however, only up to 75% of the trace cesium was adsorbed and the adsorption was nearly independent of pH over a wide range. When the concentration of cesium and competing ion was at 50% of the soil ion exchange capacity, competing cation depressed cesium adsorption by soil in the order: $H > La \geq Sr > Na > NH_4$.

At 1% of the soil capacity and lower cesium concentration, competing cation effects on cesium adsorption were slight. Trace concentrations of cesium were adsorbed to a greater degree and were more difficult to displace from the soil by competing cations than when the cesium was adsorbed in greater concentrations. The presence of small amounts of mineral phases in the soil with high cesium selectivities may account for this behavior (Ames, 1959; Jacobs and Tamura, 1960; Tamura and Jacobs, 1960; Schultz et al., 1960; Sawhney, 1964; Gaudette et al., 1966). Mica-like minerals such as illite tend to "fix" cesium. When expanded layer silicates were collapsed to a 10 Å mica spacing by potassium saturation and heating, increased cesium selectivity resulted (Tamura and Jacobs, 1961; Tamura, 1963; Coleman et al., 1963). Some researchers have considered the exchange of trace cesium on 10 Å spaced minerals to be irreversible (Klechkovski and Gulyakin, 1958; Spitsyn et al., 1963), but the reverse rate may only be much slower than the adsorption rate (Routson, 1973).

Several authors have determined cesium distribution coefficients between various solutions and rocks. These are listed in Table 3-19. Others have determined adsorption isotherms on several natural materials, and from the isotherms, derived thermodynamic functions for the specific cation exchange reactions. Some of the thermodynamic studies include Thomas (1967), Tamers and Thomas (1960), Merriam and Thomas (1956), Gaines and Thomas (1953), Lewis and Thomas (1963) and Eliason (1966) on cesium ion exchange on systems of cations with clays. Ames (1959), Frysinger (1962) and Howery and Thomas (1965) studied ion exchange and cesium thermodynamics on the natural zeolite clinoptilolite.

Prout (1958) studied the effects of system variables on Savannah River soil (80% sand, 20% clay) uptake (Kd values) for trace cesium, strontium and plutonium. The pH and adsorbed ion concentration were some of the variables examined. Cesium adsorption fell off rapidly with pH at less than 6 and decreased as more than 10% of the soil cation exchange capacity was occupied by cesium.

Berak (1963) has contributed much of the cesium adsorption work on different rock types and minerals. The standard equilibrating solution used is given in Table 3-20. Carrier cesium 1×10^{-5}M as CsCl was used along with the

TABLE 3-19. CESIUM DISTRIBUTION COEFFICIENTS FOR SEVERAL ROCKS, MINERALS AND SOIL TYPES

Medium	CsKd, ml/g	Condition	Reference
Alluvium Central Nevada	121-3165	500-4000 μm	Nork et al., 1971
Desert Alluvium Hot Creek Valley, Nevada	70-2640	500-4000 μm	Nork and Fenske, 1970
Tuff, Rainier Mesa, NTS, Nevada	1020	>400 μm	Nork and Fenske, 1970
Tuff, Rainier Mesa, NTS, Nevada	12,100-17,800	100-200 mesh	Goldberg, et al., 1962
Carbonate, Yucca Flat, NTS, Nevada	13.5	>4000 μm	Nork and Fenske, 1970
Granodiorite, Climax Stock, NTS, Nevada	8-9	100-200 mesh	Beetem et al., 1962
	1030-1810	0.5-1.0 mm	
Alluvium, INEL, Idaho	285-360	(Laboratory soil)	Schmalz, 1972
	450-950	(Field soil)	
Granite, Central Nevada	34.3	>4000 μm	Nork and Fenske, 1970
Basalt, NTS, Nevada	792-9520	32-80 mesh	Angelo et al., 1962
Basalt Amchitka Island	280	500-4000 μm	Essington and Nork, 1969
	39	500-4000 μm	
	6.5(seawater)	500-4000 μm	
Shaley siltstone New Mexico	309	>4000 μm	Nork and Fenske, 1970
Sandstone, New Mexico	102	>4000 μm	Nork and Fenske, 1970
SUPERSATURATED ROCKS (containing quartz)			
Rhyolites, Czechoslovakia	100,000	0.1-0.2 mm	Berak, 1963
	33		
	15		
	67		
	20		
	354		
	4		
	72		
	50,000		
	107		
	57		

TABLE 3-19. (continued)

Medium	CsKd, Ml/g	Condition	Reference
Central Slovakia	40		
	31		
	32		
	11		
	9		
	50,000		
	28		
	12,400		
	42		
	25		
	26		
	45		
	41		
	42		
	39		
	23		
	18		
	23		
	13		
	31		
	10		
	34		
Volcanic Glasses, East Slovakia	13	0.1-0.2 mm	Berak, 1963
	84		
	16		
	33		
Central Slovakia	72		
Iceland	12		
	6		
Rhyodacites, East Slovakia	45	0.1-0.2 mm	Berak, 1963
Dacites, Slovakia	49		
	85		
	96		
	41		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Quartz Porphyries			
Central Bohemia	52	0.1-0.2 mm	Berak, 1963
Bohemia	32		
	730		
	104		
North Bohemia	32		
SATURATED ROCKS (contain no quartz or feldspathoids)			
Trachytes,		0.1-0.2 mm	Berak, 1963
North Bohemia	89		
Slovakia	16		
Andesites, Central Slovakia	54	0.1-0.2 mm	Berak, 1963
	52		
Pyroxenic, East Slovakia	77		
	34		
	58		
	73		
	27		
Garnetic, East Slovakia	39		
Altered, East Slovakia	160		
Pyroxenic, Central Slovakia	277		
Propyllitized	56		
Granul. pyrox., vitreous	317		
Spillites, albitized	10	0.1-0.2 mm	Berak, 1963
Diabases, Bohemia	61	0.1-0.2 mm	Berak, 1963
	14		
	37		
	93		
	800		
	640		
	540		
	640		
North Moravia	19		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Melaphyres, basalt		0.1-0.2 mm	Berak, 1963
North Bohemia	1330		
	108		
	37		
Slovakia	122		
Basalts, North Bohemia,	900	0.1-0.2 mm	Berak, 1963
Vitreous	246		
	130		
	910		
	122		
	167		
UNDERSATURATED ROCKS (nonfeldspathoidal)			
Picrites, North Moravia	456 257	0.1-0.2 mm	Berak, 1963
	526		
	89		
	185		
	257		
	526		
	1330		
	456		
	30		
Teschenites with olivine, North Moravia	318	0.1-0.2 mm	Berak, 1963
	199		
	56		
	234		
	258		
	70		
Peridotite, North Moravia	96	0.1-0.2 mm	Berak, 1963
Pyroxenites. NW Bohemia	2	0.1-0.2 mm	Berak, 1963
	0		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Monchiquite, with olivine, North Moravia	95	0.1-0.2 mm	Berak, 1963
Ouachitite, with apatite North Maravia	28	0.1-0.2 mm	Berak, 1963
	52		
Olivine basalts, North Bohemia	1215	0.1-0.2 mm	Berak, 1963
	1370		
East Slovakia	1685		
Central Slovakia	75		
North Bohemia	1023		
Andesitic, Central Slovakia	170		
	185		
UNDERSATURATED ROCKS (feldspathoidal)			
Phonolites, North Bohemia	55	0.1-0.2 mm	Berak, 1963
	34		
	1150		
	1600		
Tephrites, North Bohemia			
Chabazite	594	0.1-0.2 mm	Berak, 1963
Leucite	140		
Chabazite	589		
Nepheline	517		
Nepheline-leucite	675		
Leucite	1134		
	1062		
Basanites, North Bohemia, Nepheline-leucite	397	0.1-0.2 mm	Berak, 1963
Nepheline	98		
	44		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Leucite	1550		
Nepheline	3240		
	52		
Nephelinites, NW Bohemia, Metilite	34	0.1-0.2 mm	Berak, 1963
Leucite	329		
Olivine-nepheline basalt	117		
	571		
Hauyne-nepheline basalt	700		
Leucitites, NW Bohemia	3746	0.1-0.2 mm	Berak, 1963
	1328		
	398		
Nepheline	109		
Melilitites, olive-hauyne basalt	145	0.1-0.2 mm	Berak, 1963
MINERALS			
Quartz	0	0.1-0.2 mm	Berak, 1963
Agate	2		
Chalcedony	11		
Opal	8-61		
Olivine	5		
Humite	8		
Chondrodite	0		
Thaumasite	16		
Leucophanite	2		
Zircon	3		
Topaz	4		
Kyanite	43		
Sillimanite	3		
Staurolite	1		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Garnet, alamandine	0		
Garnet, grossular	3		
Garnet, andradite	0		
Garnet, uvarovite	5		
Hydrogarnet	54		
Vesuvianite	16		
Sphene	3		
Rinkite	9		
Axinite	0		
Hemimorphite	6		
Beryl	7		
Dioptase	8		
Tourmaline	3		
Wollastonite	0		
Rhodonite	3		
Hypersthene	18		
Aegirine	50		
Augite	14		
Diopside	6		
Enstatite	1		
Jeffersonite	4		
Tremolite	8		
Chrysotile	0		
Sepiolite	900		
Attapulgite	89		
Polygorskite	150		
Zoisite	33		
Talc	0		
Pyrophyllite	8		
Biotite	21		
Muscovite	15		
Penninite	2		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Delessite	4070		
Sericite	21		
Illite	400		
Glauconite	87		
Celadonite	84		
Serpentine	17		
Kaolinite	45		
Halloysite	81		
Allophane	276		
Hisingerite	257		
Smectites	4900		
	2400		
	355		
	425		
	545		
	377		
	345		
Nontronite	388	0.1-0.2 mm	Berak, 1963
Apophyllite	8		
Melilite	68		
Feldspars		0.1-0.2 mm	Berak, 1963
Orthoclase	9		
Sanadine	58		
	6		
Albite	9		
Oligoclase	12		
Andesine	28		
Laboradorite	24		
Scapolite	26		
Leucite	56		
Analcite	54		
Pollucite	5		
Nepheline	20		
Sodalite	8		

TABLE 3-19. (continued)

Medium	CsKd, ml/g	Condition	Reference
Cancrinite	67		
Zeolites:			
Mordenite	25,000	0.1-0.2 mm	Berak, 1963
Stilbite	19,900		
	193		
Heulandite	1230		
Faujasite	230		
Harmotome	416		
Phillipsite	9900		
Chabazite	4900		
Natrolite	20		
Scolecite	9		
Thomsonite	7050		
Clinch River, TN bottom sediments	2326 - 1 hr 50,152 - 3 days 88,048 - 7 days	pH 6	Carrigan, et al, 1967
	3169 - 1 hr 50,152 - 3 days 82,769 - 7 days	pH 9	
Silty Clay, ID	3000	Quartz, illite, apatite	Wilding and Rhodes, 1963
Sandstone, fine light gray	139 166 389	4000 μm 500 μm <62 μm	Sokol, 1970
Shaley siltstone, carbonaceous, black	309 472 541	4000 μm 500 μm <62 μm	Sokol, 1970
Sandstone, fine light gray	102 141 298	4000 μm 500 μm <62 μm	Sokol, 1970
Sandstone, very fine, silty, dark gray	346 456 630	4000 μm 500 μm <62 μm	Sokol, 1970

tracer cesium. A 1% solid suspension was equilibrated for 1 day at 20°C. Results indicated that the secondary silicates (clays, zeolites) removed cesium from solution much better than the primary silicates (feldspars, quartz, etc.).

TABLE 3-20. THE EQUILIBRATING SOLUTION COMPOSITION PLUS TRACE ^{137}Cs THAT WAS UTILIZED IN ALL OF BERAK'S (1963) Kd WORK WITH 24 HOUR EQUILIBRATIONS AT 20°C

Ions	mg/l
Ca^{2+}	80.2
Mg^{2+}	12.2
Na^{+}	23.0
SO_4^{2-}	96.0
NO_3^{-}	62.0
Cl^{-}	35.4
HCO_3^{-}	61.0

Jacobs (1962) used vermiculite to illustrate the favorable 10 Å spacing caused by potassium added to the cesium in the influent solution. Cesium selectivity (Kd) increases through a maximum while the cation exchange capacity of the vermiculite decreases as shown in Table 3-21.

TABLE 3-21. EFFECT OF ADDITION OF POTASSIUM TO THE INFLUENT ON THE SORPTION OF CESIUM BY VERMICULITE FROM 0.5M $NaNO_3$ CONTAINING THE MASS EQUIVALENT OF 2 μc ^{137}Cs/ml (JACOBS, 1962)

Potassium Concentration, M	CsKd, ml/g	Final CEC, meq/100 g
0	154	75.4
0.0001	147	74.9
0.001	137	70.2
0.01	357	60.0
0.02	483	38.1
0.03	695	26.2
0.04	727	17.9
0.05	634	15.3
0.08	373	9.1
0.10	265	8.6

The cation exchange capacities of five standard clays and seven soil samples were determined using cesium, ammonium and manganese ions by Beetem et al. (1962). These authors preferred the use of cesium chloride-^{137}Cs to accurately determine clay and soil capacities for samples as small as 30 mg.

Rhodes and Nelson (1957) studied the effects of pH and sodium nitrate concentrations on cesium distribution coefficients using a glaciofluviatile silty sand composite recovered from Hanford wells. The results are given in Tables 3-22 and 3-23. In high salt solutions cesium Kd values were much less affected by pH variations than cesium tracer in water only.

TABLE 3-22. EFFECT OF pH ON ^{137}Cs ADSORPTION. SOIL WAS A COMPOSITIE GLACIOFLUVIATILE SILTY SAND FROM HANFORD, WASHINGTON. (RHODES AND NELSON, 1957)

	CsKd, ml/g	
pH	H_2O	NaCl, 4M
0.4	36.5	14.0
1.8	138.0	12.2
3.7	200	17.4
4.9	>200	18.0
7.0	>200	18.0
7.8	>200	12.0
8.5	>200	16.0
10.1	>200	18.8

TABLE 3-23. EFFECT OF $NaNO_3$ CONCENTRATION ON ^{137}Cs ADSORPTION. SAME COMPOSITE GLACIOFLUVIATILE SOIL WAS USED AS IN TABLE 3-20 (RHODES AND NELSON, 1957)

$NaNO_3$,M	CsKd, ml/g
0.25	245
0.50	195
1.0	100
2.2	50
3.6	30
4.8	20
6.0	18

Wahlberg and Fishman (1962) determined cesium Kd values with kaolinite, illite, montmorillonite and halloysite over a large cesium concentration range and in competition with sodium, potassium, calcium or magnesium. The type and amount of competing ions and the cesium concentration determined the cesium Kd variation with potassium having the most depressing effect.

Parsons (1962) determined a ^{137}CsKd value of 100 in sand, sandy loam, silt and humus at a groundwater pH of 5.4 to 6.6.

Janzer et al. (1962) determined cesium Kd values on a number of 100 to 200 mesh rock samples. The samples were divided into two parts. One part of the sample was equilibrated with the solution without cesium tracer, and finally with a cesium tracer plus the same solution. The other sample half was directly equilibrated with the cesium traced solution. There were minor differences between the Kd ranges of the two sample groups. The five equilibrating solutions varied from 1,000 to 45,000 mg/l in dissolved solids. Equilibration times were up to 30 days and each experiment was run in triplicate. The rock type descriptions and cesium Kd values are given in Table 3-24 as minimums for the highest dissolved solids solutions to maximums for lowest dissolved solids solutions. A membrane technique was used to keep solid and cesium traced solution phases separated.

TABLE 3-24. SUMMARY OF CESIUM Kd VALUES (JANZER ET AL., 1962)

	Kd, ml/g		
Sample Number	Minimum	Maximum	Rock Description
45	613	10,300	Sandstone, calcite cement
95	1,034	13,400	Siltstone, sandy
320	9	48	
331	841	15,530	
350	27	170	Gypsum rocks and siltstone
365	36	1,140	
380	445	6,657	Dolomite
479	419	3,600	Gypsum rock
510	51	2,824	Dolomite
526	1,176	8,990	
552	536	7,150	
620	661	8,250	Siltstone, silty sandstone, dolomite cement
653	302	3,766	
680	396	5,280	Gypsum rock, siltstone, sandstone

Baetsle et al. (1964) reported several cesium Kd values as a function of pH and water composition for Mol, Belgium, soil. The Kd values are given in Table 3-25 and may be directly compared with strontium Kd values on the same soils. The causes of the low deionized water Kd value relative to the cesium Kd values with mains (tap?) water are not known. Mercer (1967) gave cesium Kd values as a function of sodium and calcium normality for clinoptilolite, a natural zeolite. The Kd values varied from about 5 x 10^3 ml/g at 0.1N NaCl to about 3 x 10^5 ml/g at 0.001N NaCl. At 0.001N $CaCl_2$ the clinoptilolite cesium Kd value was about 3 x 10^5 ml/g and 3 x 10^4 ml/g at 0.1N $CaCl_2$. Certain of the secondary silicates, such as some of the zeolites, efficiently remove cesium from solution even when the concentrations of competing ions are relatively large. Rancon (1967) reported cesium Kd values of 21,000 on illite, 300 on kaolinite and 2000 ml/g on montmorillonite.

TABLE 3-25. VARIATION OF TRACE CESIUM Kd VALUES WITH pH (BAETSLE ET AL., 1964)

	Kd, ml/g			
Soil Type	Deionized Water, pH4	Mains Water, pH7.7	Mains Water, pH3	Groundwater, pH4
Eolian Sand				
Horizon A	25-38	51	224	10.1
Horizon B	31-32	145	68	-
Horizon C	226	89	79	-
Mol White Sand	50	30	-	1.3-3.2
Mol Lignitic Sand	-	3.9-7.1	-	3.4-4.3

Ames and Hajek (1966) statistically analyzed cesium adsorption data. Hajek and Ames (1968) also showed the problems associated with determining cesium distribution coefficients on the A horizon of Burbank loamy fine sand without first equilibrating the soil with the solution minus the cesium tracer. The resulting cesium Kd values depend on the solution to soil ratio used in the equilibration, as seen in Tables 3-26 and 3-27.

A curve for trace cesium loading on a 1 g Burbank soil is also given. Even these small columns, when used for Kd determinations, should be pre-equilibrated with the solution minus the radioactive tracer.

TABLE 3-26. SOLUTION:SOIL RATIO EFFECT ON TRACE CESIUM EQUILIBRIUM DISTRIBUTION COEFFICIENTS (HAJEK AND AMES, 1968)

	CsKd, ml/g			
	Solution:Soil			
Solution	100	50	10	5
Groundwater (150 mg cations/l)	8996	3538	1050	326
3N $NaNO_3$	466	380	271	206
0.5N NaCl	1091	1445	1354	1173
0.5N $CaCl_2$	5211	5362	2420	1260

TABLE 3-27. CESIUM EQUILIBRIUM DISTRIBUTION COEFFICIENTS FOR SAND, SILT AND CLAY FRACTIONS OF BURBANK LOAMY FINE SAND IN 0.5N NaCl (HAJEK AND AMES, 1968)

CsKd, ml/g								
Clay			Silt			Sand		
Solution:Soil			Solution:Soil			Solution:Soil		
500	200	100	50	10	5	50	10	5
6557	6008	5364	548	472	408	1657	1014	893

Three soils representative of the Hanford Site, the Ritzville silt loam, Burbank loamy sand and Ephrata sandy loam, were studied in detail for their ion exchange properties with cesium (Routson, 1973). The three soils were thoroughly characterized in terms of their physical properties (size fractionation), chemical properties (exchangeable Ca, Mg, Na and K in each soil horizon and the total cation exchange capacity of each) as well as their mineralogical properties (semiquantitative mineralogy of each size fraction, plus organic carbon and calcite content of each fraction). Cesium equilibrium distribution coefficients from 0.2N NaCl were determined on the "as received" soil horizon samples, sodium-based horizon samples and horizon samples with organic carbon removed, calcite removed and both removed. The results are given in Table 3-28. Soil samples were pre-equilibrated with a 0.2N NaCl except for the "as received" cases. The Ritzville soil averaged about 12 meq/100 g, the Ephrata soil about 7 meq/100 g and Burbank about 5 meq/100 g cation exchange capacities. The Kd values were directly correlated with the soil cation exchange capacities.

TABLE 3-28. TRACE CESIUM ADSORPTION BY THREE HANFORD SOILS FROM A 0.2N NaCl SOLUTION (ROUTSON, 1973)

	As Received	Na-based	Organic C Removed	Calcite Removed	Organic C+ Calcite Removed
Ritzville					
A_{12}	4869	4869	2750	5980	4069
B_1	4332	4930	2154	6486	3152
C_{ca}	3111	5455	2608	4060	2592
C	3529	6169	3510	5174	2578
Burbank					
A_{12}	2775	1964	2467	2540	3024
AC	2680	2571	2682	2448	2338
AC_2	2573	3533	2513	2070	2036
IC	1588	1633	1155	1478	1010
Ephrata					
A_{12}	3941	2385	3027	5230	2671
B_1	4696	2410	2835	4071	2901
IB_2	3491	1950	2402	2316	1850
IIC	1919	1553	2012	2423	836

R. J. Serne of PNL, 1973, also determined cesium distribution coefficients from high salt, high pH solutions. The solution compositions and sediments are the same as those described in Table 3-9 and 3-10. The results of the high salt work are provided in Table 3-29. Each cesium Kd was determined in triplicate. The values given in Table 3-29 represent the average of the three Kd values.

TABLE 3-29. CESIUM Kd VALUES BETWEEN SEVEN GLACIOFLUVIATILE SEDIMENTS AND THE SOLUTIONS OF TABLES 3-9 AND 3-10

Sediments	Solution I	II	III	IV	V
1	13.41	6.00	1.80	0.85	12.02
2	9.37	3.47	1.37	0.61	7.14
3	9.06	3.42	1.27	0.58	7.21
4	8.11	3.08	1.37	0.73	7.68
5	10.93	3.70	1.83	2.92	11.30
6	7.88	2.04	0.93	1.20	7.97
7	8.74	2.79	1.14	1.47	9.49

Migration Results

Field Studies--

Mawson (1956) and Evans (1958) reported the results of studies on the movement of fission products disposed to ground in a sand at Chalk River, Ontario. The rate of movement was followed with a series of wells from which groundwater samples were collected and analyzed. Cesium moved the least and at the lowest velocity of several radionuclides including strontium, cerium and ruthenium in dilute, neutral wastes. Cesium was also the slowest radionuclide to move in acid wastes as well because neutralization was soon accomplished due to soil buffering.

The drilling of core wells into abandoned covered trench disposal sites at Hanford was used to determine cesium distribution in the field. Raymond (1965) found that the bulk of the ^{137}Cs was contained in the upper 3 ft beneath the disposal site.

Brown (1967) reviewed the hydrology and geology of the Hanford areas and gave well profiles of ^{137}Cs at two disposal sites. Anomalies in the radionuclide distribution were correlated with stratigraphic features such as a caliche ($CaCO_3$) bed and a loess lens. The average rate of downward moisture movement decreased from 1.5 m/yr in 1958 to 1959 to 0.5 m/yr from 1963 to 1966, as a result of disposal site retirement in 1956. A study to determine ^{137}Cs

leaching by groundwater of contaminated soils from core wells showed that 50 column volumes were required to leach 11% of the ^{137}Cs. Another 450 column volumes removed an additional 4% of the ^{137}Cs. Trace ^{137}Cs was added to the groundwater. Distribution coefficients on sediments from below the groundwater table were 300 ml/g for ^{137}Cs. Eight relatively long-lived radionuclides were detected in the groundwater including ^{137}Cs. ^{137}Cs was adsorbed in the upper 10 m of 216-S-1 and -2 covered trenches. About 1.5 x 10^8 liters of low salt wastes containing about 2000 Ci of ^{137}Cs were disposed to 216-S-1 and -2 prior to shutdown in 1956.

Haney (1967) reported the disposition of ^{137}Cs in the 216-BY covered trenches that had received 3.4 x 10^7 liters of U-Plant high salt scavenged waste that contained 4.1 x 10^5 Ci of undifferentiated β emitting radionuclides including 3300 Ci of ^{137}Cs. The 8 BY Covered trenches were in service from December 1954 to December 1955 at Hanford. Monitoring and sampling wells drilled into and near the ground disposal facility showed that the cesium peak occurred at 28.7 μCi/g soil at about 3 meters below the bottom of the trench and rapidly decreased with depth. Approximately 12,900 Ci of ^{90}Sr also were contained in the waste. The ^{90}Sr peak soil loading occurred at about 5 meters below the bottom of the trench. Groundwater at the site was 67 m below ground surface. Soil samples below 23 m contained less than 2 x 10^{-3} μCi/g of either cesium or strontium.

The migration of ^{137}Cs from Oak Ridge seepage pits was studied by Lomenick et al. (1967). It was found that most of the ^{137}Cs in the pits was tied up in an illitic clay sludge. Water movement was found to be 0.15 m/day while ^{137}Cs movement was 0.127 cm/yr.

Magno et al. (1970) determined radionuclide migration through the effluent lagooning system of the Nuclear Fuel Services plant in Western New York. From their analytical data, they estimated that 75% of the ^{134}Cs and ^{137}Cs discharged from the plant were deposited in the sediments in the lagoon system. From 40 to 95% of the cesium at the lagoon system exit was associated with suspended solids.

In 1973, the 241-T-106 underground liquid high level waste storage tank at Hanford leaked about 435,000 liters of waste into the surrounding sediments (Anon., 1973). A series of wells were drilled to ascertain the locations and movements of the various radionuclides in the sediment column. Monitoring and core sample analysis showed the relative mobilities of the radionuclides in the 1M NaOH, 5M $NaNO_3$ solution. Plutonium was the least mobile, but cesium mobility was only slightly more rapid. None of the radionuclides migrated below 27 m. The water table was at 62 m depth.

Brookins et al. (1975) and Brookins (1976) have reported that a study of the ^{135}Ba and ^{137}Ba daughters of ^{135}Cs and ^{137}Cs found at the prehistoric natural reactor site at Oklo in Gabon indicate the probable retention of fission product cesium at the reactor site.

Laboratory Studies--

Nishita et al. (1960) studied the effects of potassium and cesium on the release of ^{137}Cs from three soils to plants. Addition of potassium was found to be inefficient in reducing ^{137}Cs uptake by plants. The addition of nonradioactive cesium always increased plant uptake of ^{137}Cs, even when the cesium level was injurious to the plant.

Davis (1961) reported that the soil exchange capacity was essentially constant above pH 3.5. Cesium was most effectively desorbed from soils by neutral salts, and more readily by potassium than by sodium or calcium. Trace amounts of cesium were held more strongly by soils than trace amounts of strontium.

Nishita et al. (1962) used an equilibrium method in a followup study to determine the effects of stable cesium and potassium on the movement of tracer quantities of ^{137}Cs and ^{42}K. The concentration of stable cesium and potassium was an important factor. When ^{137}Cs was only a negligible fraction of the cesium in solution, only a negligible fraction of ^{137}Cs was adsorbed. In equimolar mixtures of cesium and potassium, the adsorption of cesium relative to potassium decreased as the ionic strength increased. In low concentrations, cesium was more effective than potassium in releasing ^{137}Cs from soils. In high concentrations, potassium can be as effective as cesium in releasing ^{137}Cs.

The adsorption of cesium by soils and its displacement by salt solutions were investigated by Coleman et al. (1963). Montmorillonite, illite and kaolinite loaded with cesium were readily leached by 1N KCl or 1N $CaCl_2$.

Vermiculite and heated (600°C for 12 hr) potassium montmorillonite bound cesium tightly while contacting solutions of $CaCl_2$ and $AlCl_3$ but not KCl or NH_4Cl solutions. Prolonged leaching with 1N KCl removed 97.5% of the cesium adsorbed on heated potassium montmorillonite while 1N $CaCl_2$ replaced 88%. The exchange-displacement behavior of cesium suggests that its adsorption in interlayer spaces allows admission of potassium and ammonium ions but restricts the entry of calcium. Apparent specific adsorption of cesium against exchange with $CaCl_2$ occurred at large cesium concentrations.

Miller and Reitemeier (1963) published some of their earlier work on strontium leaching adding some additional cesium leaching work. Leaching treatments consisted of applications of 30 and 300 in. of deionized water, 0.005N NaCl and 0.005N $CaCl_2$. There was little downward movement of cesium. Assays showed that 96.6 to 100% of the ^{134}Cs was in the surface 1.4 in. of the soil columns (Norfolk loamy sand, Hagerstown silt loam, Fort Collins loam, Miami silt loam, Huntley clay) after 300 in. of leaching by the above solutions.

Cesium K values for ^{134}Cs in the saturated subsoil at Mol, Belgium, also were given by Baetsle et al. (1964). The K values are listed in Table 3-30 and may be compared with similar values obtained on the same soils for ^{89}Sr and ^{152}Eu. Mol sand is nearly pure quartz. The effect of pH on cesium migration in relation to water can be seen in the K values. In all cases, except for the perturbed profile, K values decreased (cesium mobility increased in relation to water velocity) as the pH decreased. K values are markedly different even with single pH unit.

Cesium distribution coefficients at pH 3 and the rate of cesium movement in relation to the groundwater movement in Houthulst clays are given in Table 3-31. These values may be compared for the same soil samples with ^{89}Sr and ^{152}Eu. Note that the K values for cesium decreased in the Houthulst clays by an order of magnitude as compared to the Mol sands. It is unfortunate that the minerals constituting the Houthulst clays were not specified.

Carlile and Hajek (1967) reported an example of physical transport through a soil column. About 0.1% of the ^{137}Cs was found in 2 cm diameter by 40 cm length N-Area Hanford soil columns. Until 5 column volumes of

TABLE 3-30. K VALUES OF CESIUM IN THE SATURATED SUBSOILS AT MOL, BELGIUM (BAETSLE ET AL., 1964). K IS DEFINED ON PAGE 2-30.

Soil Types	K	
	pH4	pH3
Mol sand	9	6
Perturbed profile	125	431
Mol sand + eolian sand	-	24
Mol sand + lignite	76	20
Mol sand	38	26
Mol sand	48	32
Mol sand	55	19
Mol sand	38	14
Mol sand	31	15
Mol sand	25	13

TABLE 3-31. CESIUM DISTRIBUTION COEFFICIENTS AND RELATIVE MIGRATION RATES IN HOUTHULST CLAYS AT pH 3 (BAETSLE ET AL., 1964)

		Core Well I			
Depth, m	Kd, ml/g	K	Depth, m	Kd, ml/g	K
0-1	111.5	372	10-11	198	560
1-2	77.0	257	11-12	295	983
2-2.5	83.0	278	12-13	386	1286
2.5-3	47.7	160	13-14	475	1583
3-4	-	-	14-15	427	1423
4-5	145.2	485	15-16	742	2472
5-6	133.5	466	16-17	765	2548
6-7	107.0	357	17-18	484	1613
7-8	-	-	18-19	470	1566
8-9	103	344	18-19	250	834
9-10	163	543			
		Core Well II			
0-1	-	-	10-11	536	1786
1-2	31	104	11-12	527	1756
2-3	29	98	12-13	664	2212
3-4	165	550	13-14	374	1246
4-5	342	1140	14-15	247	824
5-6	570	1899	15-16	291	970
6-7	693	2309	16-17	158	527
7-8	494	1646	17-18	220	733
8-9	462	1536	18-19	193	644
9-10	441	1470	19-20	241	804

Columbia River water (dissolved solids = 119 mg/l) had passed through the soil, leakage did not fall below detection limits (10^{-3}% leakage). Effluent samples were centrifuged, treated with hydrogen peroxide to destroy organic material, and recentrifuged. The peroxide treatment did not affect cesium removal by centrifugation, which removed 50 to 75% of the cesium in either case. It was found that the low ionic strength river water dispersed the soil colloids on which the ^{137}Cs was adsorbed. The breakthrough of cesium continued until the colloids were flushed from the column. Preleaching with river water rid the soil columns of colloids and resulted in no initial cesium leakage.

Eichholz et al. (1967) investigated the partitioning of dissolved radionuclides between suspended sediment particles and aqueous solutions. Their work does not necessarily have a direct application to particulate migration through soils, but it does give a feeling for the types and amounts of radionuclides that can be transported on suspended solids. Several bodies of water were sampled and utilized by the authors in the adsorption study as sources of suspended solids. Some of the properties of the natural water samples are listed in Table 3-32. A fission product mixture was added; the system allowed to come to equilibrium; and the water was recovered and passed through a mixed bed ion exchange resin. The resin and sediment were then counted with the radionuclides extraction results shown in Table 3-33. It is noteworthy that a large portion (80 to 90%) of the radionuclides was associated and traveled with the particulate matter in a highly concentrated form. There is a direct correlation between cesium adsorption and the suspended solids concentration, with some effect of dissolved solids in the water.

Levi and Miekeley (1967) reported that experiments with vermiculite and the cesium fixation phenomenon showed that a lattice contraction was not responsible for cesium uptake as previously suggested by others. Cesium fixed with respect to isotopic exchange was shown to become mobile by exchange with many other ions. Two different "defixation" mechanisms were indicated, one caused by strongly hydrated ions and the other by small nonhydrated ions. Cesium ions can be exchanged for potassium, but not potassium ions for cesium. Strontium isotopic exchange curves were obtained with mixed Cs-Sr vermiculite. Strontium ions can be exchanged in the system but at a reduced rate in their

TABLE 3-32. PROPERTIES OF NATURAL WATER SAMPLES (EICHHOLZ ET AL., 1967)

Source	Suspended Solids, ppm	Dissolved Solids, ppm	pH	Conductivity μmhos	Solids Composition
Colorado River, Utah	229	350	7.5	540	95% quartz, 5% calcite, feldspar, illite, kaolinite
Camp McCoy, Wisconsin	12	60	6.9	80	30% quartz + feldspar, 6% kaolinite, 24% illite
Bayou Anacoco, Lousiana	24	63	6.2	60	30% quartz, 2% kaolinite, 6% smectite
Lodgepole Creek Nebraska	965	200	6.8	300	20% illite, 80% smectite
Chattahoochee River, Georgia	131	31	7.3	45	33% quartz, 44% kaolinite 23% illite
Billy's Lake Georgia (swamp)	8	68	4.2	45	2% quartz, balance was amorphous and/or organic

TABLE 3-33. ADSORPTION OF RADIONUCLIDES ON SUSPENDED SOLIDS (EICHHOLZ ET AL., 1967)

Source	^{137}Cs, %
Colorado River	83.9
Camp McCoy	3.3
Bayou Anacoco	16.2
Lodgepole Creek	96.3
Chattahoochee River	26.1
Billy's Lake	0.3

mobility. The authors suggest that it may be possible to slow migration of various radionuclides in soils by mixing them with cations fixed like cesium in vermiculite.

Nishita and Essington (1967) continued work on the effects of chelating agents on ^{89}Sr, ^{91}Y, ^{106}Ru, ^{137}Cs and ^{144}Ce migration in different types of soils. Movement by water leaching, irrespective of soils, was in the order

^{137}Cs, ^{91}Y, ^{144}Ce < ^{89}Sr << ^{106}Ru. Except in the Hanford sandy loam (a California soil), practically no movement in ^{137}Cs, ^{91}Y or ^{144}Ce occurred by water leaching. EDDHA was generally the least effective, while the effectiveness in promoting leaching of DTPA and EDTA varied with the soil type and radionuclide. Soil pH probably had a large effect on complexing agent effectiveness, but the causes were not determined.

Knoll (1969) reported that two waste organic solutions had detrimental effects on retention of radionuclides by the soil. One was a mixture of 0.4M di-(2-ethythexyl) phosphoric acid and 0.2M tributyl phosphate in paraffin hydrocarbons (C_{10} to C_{14}), and the other was hydroxyacetic acid. With the 0.4M D2EHPA-0.2TBP solution, strontium removal from a 5.0 cm^3 soil column was 70% at 10 column volumes. Only about 12% of the cesium was removed in the same throughput, as was 80% of the adsorbed americium and 30% of the plutonium. With a 0.25M hydroxyacetic acid solution, pH 3.7, plutonium, strontium and americium removal was essentially complete at 10 column volumes. As the concentration of hydroxyacetic acid decreased, the migration rate of the strontium, plutonium and americium also decreased. None of the cesium on the column was eluted at any of the hydroxyacetic acid concentrations.

Salo and Saxen (1974) investigated the role of humic substances in the transport of radionuclides. Atomic absorption and X-ray fluorescence were used to determine the stable elements bound to the humic materials fractionated into different molecular size groups. Surface waters from Bothnian Bay, Finland, were used to study the molecular size distributions of humic substances, and Kd values were determined by gel chromatography. The distribution of strontium and cesium into different molecular size groups of the humic substances were discussed. Cesium concentration was directly correlated with the colored colloids, unlike the strontium, manganese and zinc. It was postulated that the cesium was adsorbed on the colored colloids. A wavelength of 350 mm was used to determine color intensity.

Summary

Cesium mainly exists in solutions as Cs^+. Therefore, the principal reaction mechanism of cesium adsorption on soils and rocks is expected to be cation exchange. In some instances cesium shows a direct Kd-cation exchange capacity relationship (Routson, 1973), and in other instances, no relation between Kd and exchange capacity (Jacobs, 1962). At trace cesium concentrations competing cation effects are minor (McHenry, 1954), while at 10% or more of the exchange capacity occupied by cesium, the Kd value beings to fall off (Prout, 1958). Potassium is better than sodium or calcium for desorbing cesium (Davis, 1961). There is a tendency for cesium to become "fixed" in 10Å mica-like minerals (Tamura and Jacobs, 1961; Jacobs, 1962; Tamura, 1963; Coleman et al., 1963; Lomenick, 1967), which may be due to a slow desorption rate rather than fixation (Levi and Miekeley, 1967; Routson, 1973). The secondary silicate minerals such as zeolites and clay minerals generally show much higher cesium Kd values than the primary silicate minerals found in igneous rocks (Berak, 1963).

The migration rate of cesium in the groundwater is faster at lower pH values but slower through clays than through sands due to larger clay Kd values (Baetsle et al., 1964). Much of the cesium that migrates in surface waters does so adsorbed on suspended solids (Eichholz et al., 1967; Magno et al., 1970).

Occasionally cesium can migrate through the soil column adsorbed on suspended solids (Carlile and Hajek, 1967). Chelating agents and organic soil materials have little affect on cesium migration through soils (Nishita and Essington, 1967; Knoll, 1969; Salo and Saxen, 1974).

References

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Ames, L. L., Jr. 1959. Zeolite Extraction of Cesium from Aqueous Solutions. HW-62607.

Ames, L. L., Jr. and B. F. Hajek. 1966. Statistical Analysis of Cesium and Strontium Sorption on Soils. BNWL-CC-539.

Angelo, C. G., N. C. Goldberg, V. J. Janzer, and W. A. Beetem. 1962. Summary of Kd's for Fission Products Between Ground Water and Basaltic Rocks. IN: Geology of the U18a Site, Buckboard Mesa, NTS Part VI. U.S.G.S. Report Project Danny Boy, WT 1828. pp. 66-81.

Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Baetsle, L. H., P. Dejonghe, W. Maes, E. S. Simpson, J. Souffriau, and P. Staner. 1964. Underground Radionuclide Movement. EURAEC-703.

Beetem, W. A., V. J. Janzer, C. G. Angelo, and M. C. Goldberg. 1962. Summary of Distribution Coefficients for Fission Products Between Ground Water and Granite Rocks, Climax Stock, NTS. U.S.G.S. Technical Letter NTS-13.

Berak, L. 1963. The Sorption of Microstrontium and Microcesium on the Silicate Minerals and Rocks. UJV-528-63.

Bertrand, G. and D. Bertrand. 1949. Sur la Presence et la Teneur en Cesium des Terres Arables. Compt. Rend. 229:533-535.

Beus, A. A. and E. A. Fabrikova. 1961. Distribution of Cesium in the Granites of the USSR. Geochemistry. 1961-970-976.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brookins, D. G., M. J. Lee, B. Mukhopadahyay and S. L. Bolivar. 1975. Search for Fission-Produced Rb, Sr, Cs and Ba at Oklo: in IAEA Symp. 204, p. 401-414.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Carlile, B. L. and B. F. Hajek. 1967. Soil Radionuclide Adsorption and Particulate Filtration in an N-Area Soil. BNWL-CC-995.

Carrigan, P. H., Jr., R. J. Pickering, T. Tarmura, and R. Forbes. 1967. Radioactive Materials in Bottom Sediment of Clinch River: Part A. Investigations of Radionuclides in Upper Portion of Sediment. ORNL-3721, Suppl. 2A.

Charlot, G. 1957. Qualitative Analysis and Solution Reactions. Fourth Edition. Masson, Paris.

Coleman, N. T., R. J. Lewis, and D. Craig. 1963. Sorption of Cesium by Soils and its Displacement by Salt Solutions. Soil Science Society of America, Proceedings. pp. 290-294.

Davis, J. J. 1961. Cesium and Its Relationships to Potassium in Ecology. IN: Radioecology. V. Schultz and A. W. Klement (eds.). pp. 539-556.

Eichholz, G. G., T. F. Craft, and A. N. Galli. 1967. Trace Element Fractionation by Suspended Matter in Water. Geochim. et Cosmochim. Acta. 31:737-745.

Eliason, J. R. 1966. Montmorillonite Exchange Equilibria with Strontium-Sodium-Cesium. Am. Mineral. 51:324-335.

Essington, E. H. and W. E. Nork. 1969. Radionuclide Contamination Evaluation - Milrow Event. NVO-1229-117.

Evans, E. J. 1958. Chemical Investigations of the Movement of Fission Products in Soil. CRER-792.

Frysinger, G. R. 1962. Cesium-Sodium Ion Exchange on Clinoptilolite Nature. 194:351.

Gaines, G. L. and H. C. Thomas. 1953. Adsorption Studies on Clay Minerals. II. A Formulation of the Thermodynamics of Exchange Adsorption. J. Chem. Phys. 21:714-718.

Graudette, H. E., R. E. Grim, and C. F. Metzger. 1966. Illite: A Model Based on the Sorption Behavior of Cesium. Am. Mineral. 51:1649-1656.

Goldberg, M. C., V. J. Janzer, C. G. Angelo, and W. A. Beetem. 1962. The Effect of Sodium Ion Concentration on Distribution Coefficients for Tuffs from NTS. U.S.G.S. Technical Letter NTS-16.

Hajek, B. F. and L. L. Ames, Jr. 1968. Trace Strontium and Cesium Equilibrium Distribution Coefficients: Batch and Column Determinations. BNWL-SA-843.

Haney, W. A. 1967. Final Report on the Effects of Ben Franklin Dam on Hanford. BNWL-412. pp. 8-10.

Heier, K. S. and J. A. S. Adams. 1964. The Geochemistry of the Alkali Metals. Phys. Chem. Earth. 5:235-380.

Hirst, D. M. 1962. The Geochemistry of Modern Sediments from the Gulf of Paria. II. The Location and Distribution of Trace Elements. Geochim. et Cosmochim. Acta. 26:1147-1188.

Horstman, E. L. 1957. The Distribution of Lithium, Rubidium, and Caesium in Igneous and Sedimentary Rocks. Geochim. et Cosmochim. Acta. 12:1-28.

Howery, D. G. and H. C. Thomas. 1965. Ion Exchange on the Mineral Clinoptilolite. J. Phys. Chem. 69:531-537.

Izrael, Yu.A. and F. Ya. Rovinskii. 1970. Hydrological Uses of Isotopes Produced in Underground Nuclear Explosions for Peaceful Purposes. UCRL-Trans-10458.

Jacobs, D. G. 1962. Cesium Exchange Properties of Vermiculite. Nuclear Sci. Eng. 12:285-292.

Jacobs, D. G. and T. Tamura. 1960. The Mechanism of Ion Fixation Using Radioisotope Techniques. IN: 7th International Cong. of Soil Sci. II: 206-214.

Janzer, V. J., M. C. Goldberg, C. G. Angelo, and W. A. Beetem. 1962. Summary of Distribution Coefficients for Fission Products Between Ground Water and Rocks from Project Gnome. IN: Hydrologic and Geologic Studies for Project Gnome. Part IV, U.S.G.S.

Klechkovskii, V. M. and I. V. Gulyakin. 1958. The Behavior in Soils and Plants of Traces of Strontium, Cesium, Ruthenium, and Zirconium. Soviet Soil Sci. 3:219-230.

Knoll, K. C. 1969. Reactions of Organic Wastes and Soils. BNWL-860.

Levi, H. W. and N. Miekeley. 1967. Studies on Ion Diffusion in Vermiculite. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/12, pp. 161-167.

Lewis, R. J. and H. C. Thomas. 1963. Adsorption Studies on Clay Minerals. VIII. A Consistency Test of Exchange Sorption in the Systems Sodium - Cesium - Barium Montmorillonite. J. Chem. Phys. 67:1781-1783.

Lomenick, T. F., D. G. Jacobs and E. G. Struxness. 1967. The Behavior of Strontium-90 and Cesium-137 in Seepage Pits at ORNL. Health Physics. 13: 897-905.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Mawson, C. A. 1956. Waste Disposal into the Ground. Proc. of the Inter. Conf. on the Peaceful Uses of Atomic Energy. 9:676-678.

McHenry, J. R. 1954. Adsorption and Retention of Cesium by Soils of the Hanford Project. HW-31011.

Mercer, B. W. 1967. Ion Exchange Equilibria of Trace Cesium-137 and Strontium-85 in Multicomponent Systems. BNWL-SA-1173.

Merriam, C. N., Jr. and H. C. Thomas. 1956. Absorption Studies on Clay Minerals. IV. Alkali Ions on Attapulgite. J. Chem. Phys. 24:993.

Miller, J. R. and R. F. Reitemeir. 1963. The Leaching of Radiostrontium and Radiocesium Through Soils. Soil Sci. Soc. Am. Proc. 27:141-144.

Nishita, H. and E. H. Essington. 1967. Effect of Chelating Agents on the Movement of Fission Products in Soils. Soil Science. 102:168-176.

Nishita, H., E. M. Romney, G. V. Alexander, and K. H. Larson. 1960. Influence of K and Cs on Release of Cs 137 from Three Soils. Soil Science. 89:167-176.

Nishita, H., P. Taylor, G. V. Alexander, and K. H. Larson. 1962. Influence of Stable Cs and K on the Reactions of Cs 137 and K 42 in Soils and Clay Minerals. Soil Science. 94:187-197.

Nork, W. E. and P. R. Fenske. 1970. Radioactivity in Water - Project Rulison. NVO-1229-131.

Nork, W. E., E. J. Forslow, and E. H. Essington. 1971. Radioactivity in Water, Central Nevada Test Area. NVO-1229-175.

Parsons, P. J. 1962. Movement of Radioactive Waste Through Soil. 5. The Liquid Disposal Area. CRER-1089.

Prout, W. E. 1958. Adsorption of Radioactive Wastes by Savannah River Plant Soil. Soil Science. 86:13-17.

Rancon, D. 1967. Mechanism of Radioactive Contamination in Consolidated Impermeable Rocks or Rocks of Very Low Permeability. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/14, pp. 179-199 (in French).

Raymond, J. R. 1965. Cesium and Strontium Distribution Beneath Liquid Waste Disposal Sites. BNWL-235.

Rhodes, D. W. and J. L. Nelson. 1957. Disposal of Radioactive Liquid Wastes from the Uranium Recovery Plant. HW-54721.

Routson, R. C. 1973. A Review of Studies on Soil-Waste Relationships on the Hanford Reservation from 1944 to 1967. BNWL-1464.

Salo, A. and R. Saxen. 1974. On the Role of Humic Substances in the Transport of Radionuclides. Report SFL-A20, Inst. Rad. Phy., Helsinki, Finland.

Sawhney, B. L. 1964. Sorption and Fixation of Microquantities of Cesium by Clay Minerals: Effect of Saturating Cations. Soil Science Society America, Proceedings. 28:183-186.

Schmalz, B. L. 1972. Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station. IDO-10049.

Schneider, K. J. and A. M. Platt (eds). 1974. High-Level Waste Management Alternatives. BNWL-1900, Volume I, Appendix 2.D, pp. 2.D.7-2.D.8.

Schulz, R. K., R. Overstreet, and I. Barshad. 1960. On the Soil Chemistry of Cesium-137. Soil Science. 89:16-27.

Sokol, D. 1970. Groundwater Safety Evaluation - Project Gasbuggy. PNE-1009.

Spitsyn, V., V. C. Balukova, and T. A. Ermanova. 1963. Studies on Sorption and Migration of Radioactive Elements in Soil. IN: Treatment and Storage of High-Level Radioactive Wastes. IAEA, Vienna, pp. 569-577 (in Russian).

Sreekumaran, C., K. C. Pillai, and T. R. Folsom. 1968. The Concentrations of Lithium, Potassium, Rubidium and Cesium in Some Western American Rivers and Marine Sediments. Geochim. et Cosmochim. Acta. 32:1229-1234.

Tamers, M. A. and H. C. Thomas. 1960. Ion-Exchange Properties of Kaolinite Slurries. J. Chem. Phy. 64:29-32.

Tamura, T. 1963. Cesium Sorption Reactions as Indicator of Clay Mineral Structures. IN: Proc. Natl. Conf. Clays, Clay Minerals. 10:389-398.

Tamura, T. 1963. Selective Ion Exchange Reactions for Cesium and Strontium by Soil Minerals. Colog. Intern. Retention Migration Ions Radioactifs Sols, Saclay, p. 95-104.

Tamura, T. and D. G. Jacobs. 1960. Structural Implications in Cesium Sorption. Health Physics. 2:391-398.

Tamura, T. and D. G. Jacobs. 1961. Improving Cesium Selectivity of Bentonites by Heat Treatment. Health Physics. 5:149-154.

Taylor, S. R. 1964. Abundance of Chemical Elements in the Continental Crust: A New Table. Geochim. et Cosmochim. Acta. 28:1273-1285.

Taylor, S. R. 1964. Trace Element Abundances and the Chondritic Earth Model. Geochim. et Cosmochim. Acta. 28:1989-1998.

Taylor, S. R. and A. J. R. White. 1966. Trace Element Abundances in Andesites. Bull. Volcanol. 29:177-194.

Thomas, H. C. 1967. The Thermodynamics of Ion Exchange on Colloidal Materials with Applications to Silicate Minerals. Thesis. University of North Carolina.

Turekian, K. K. and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Bull. Geol. Soc. America. 72:175.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.

Wahlberg, J. S. and M. J. Fishman. 1962. Adsorption of Cesium on Clay Minerals. U.S.G.S. Bulletin 1140-A.

Wilding, M. W. and D. W. Rhodes. 1963. Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho. IDO-14624.

COBALT

Natural Soil and Rock Distributions

The average cobalt concentrations found in igneous and sedimentary rocks are listed in Table 3-34. As can be seen, the cobalt content of rocks steadily decreases from the dark ultramafic rocks to the light-colored granitic rocks. The ultrabasic rocks usually contain the bulk of the cobalt in olivines and pyroxenes, but an occasional sulfide body in these rocks provides a workable ore deposit (Young 1957). Cobalt normally is enriched in areas of low redox potential in the environment.

TABLE 3-34. COBALT CONCENTRATIONS IN IGNEOUS AND SEDIMENTARY ROCKS IN ppm (YOUNG, 1957)

Igneous					Sedimentary		
		Granitic					
Ultramafic	Basaltic	High Ca	Low Ca	Syenite	Shale	Sandstone	Limestone
150	48	7	1	1	19	0.3	0.1

During weathering processes, cobalt is separated from manganese and iron because its (III) oxidation state is normally unstable unless complexed. However, certain bacteria are known to liberate chelated Co(III), as stable amino acid complexes from the soil. Little is known, as yet, of these reactions; but the technique of predicting mineral solubilities for cobalt based on thermodynamic data may not be entirely applicable if the bacterial reactions are ignored (Moore, 1964). Vinogradov (1959) reported the average soils content of cobalt as 8 ppm. Cobalt contents of up to 1.96 wt% CoO have been reported for calcite (Hacquaert, 1925).

Brief Chemistry

Only one stable cobalt nuclide, ^{59}Co, is known to exist in nature. Cobalt-60 is the principle cobalt activation product radionuclide. Cobalt oxidation states include Co(II) and Co(III). Cobalt is geochemically similar to the other ferromagnetic and closely related transition metals, iron and nickel.

Sulfides of nickel and cobalt constitute the chief cobalt ore minerals. Co^{+2} ionic radius in octahedral coordination is 0.74 Å, intermediate between

Ni^{+2} (0.70 Å) and Fe^{+2} (0.77 Å) (Shannon and Prewitt, 1969). The relative stabilities of the Co(II) and Co(III) states are greatly affected by complexing in aqueous solutions (Latimer, 1952). Although Co^{+3} cannot exist in aqueous solution, complexing can stabilize the trivalent state which would normally decompose water.

Solid Phase and Solution Equilibria

The sources for thermodynamic data for various solid phases were: Sillen and Martell (1964), $Co(OH)_3$, $CoCO_3$, CoOOH; Wagman et al. (1969), CoO, $CoHPO_4$; Robie and Waldbaum (1968), $CO_3(PO_4)_2$; Chase et al. (1975), Co_3O_4. The stability of cobalt solid phases depends on the pH and the oxidation-reduction environment. For example, in acidic (pH 6) and oxidizing (pO_2 0.68) environments, the solids in increasing order of stability are: $Co(OH)_3$, $Co(OH)_2$ pink, $CoHPO_4$, $Co_3(PO_4)_2$, $CoCO_3$, Co_3O_4, and CoOOH as shown in Figure 3-7. With the change in oxidation-reduction environment, all the minerals except $Co(OH)_3$, Co_3O_4, and CoOOH would stay in their relative positions. The latter minerals would decrease in stability. With the change in oxidation-reduction conditions from the extremely oxidizing condition to moderately well oxidized or reducing conditions, ($pO_2 > 20$), $CoCO_3$ would be the most stable mineral. Under extremely reducing conditions such as $pO_2 80$, CoS would be the most stable mineral. Cobalt sulfide (CoS) is the chief cobalt ore mineral. In general, the stability of all the cobalt minerals increases with an increase in pH.

Cobalt exists as Co^{2+} and Co^{3+} and forms solution complexes with common soil anions (OH^-, Cl^-, SO_4^{2-}, NO_3^-). The relative concentration of these solution species in equilibrium with $CoCO_3$ and in an oxidizing environment ($O_2 = 10^{-0.68}$) is depicted in Figure 3-8. If a solid phase other than $CoCO_3$ or a constant concentration of Co is chosen for the diagram, the lines will shift up and down, while the relative concentration of various solution species would stay the same. The thermodynamic data for $CoSO_4^+$ were obtained from Sillen and Martell (1964) the hydrolysis species data were obtained from Baes and Mesmer (1976). Data for all the other species were obtained from Wagman et al. (1968, 1969).

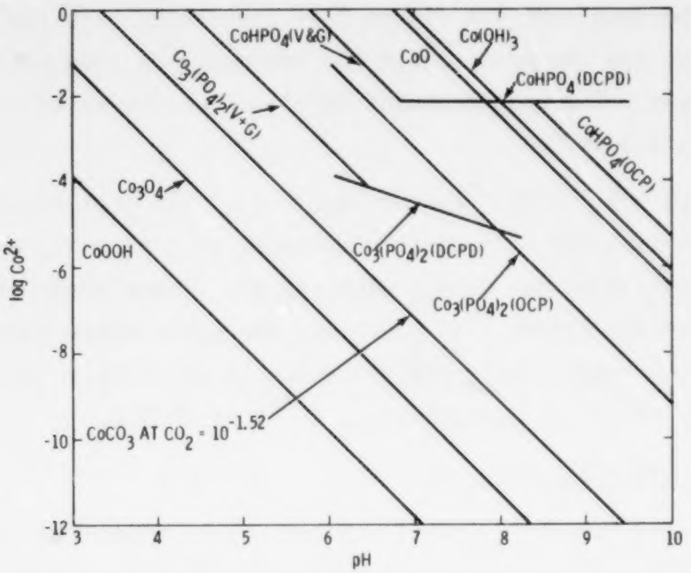

Figure 3-7. The relative stability of cobalt solids in an oxidizing soil environment [$pO_2(g)$ = 0.68 atm], pCa^{2+} = 2.5 and phosphate levels in equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP).

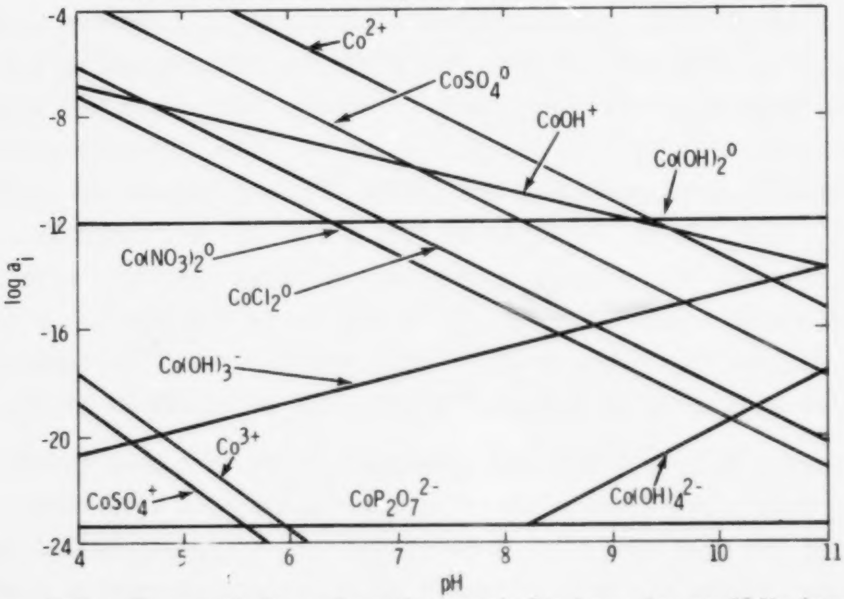

Figure 3-8. The activity of various cobalt ions in equilibrium with $CoCO_3(s)$ in an oxidizing soil environment [$pO_2(g)$ = 0.68 atm], $pCO_2(g)$ = 1.52 atm, pCl^- = pSO_4^2 = 2.5, pNO_3 = 3.0 and $pH_2PO_4^-$ = 5.0.

It can be seen from the figure that cobaltinous ion (Co^{2+}) and its solution complexes are the most stable and dominant solution species in the oxidizing environment. The most dominant solution species up to a pH value of approximately 9.5 is Co^{2+}.

Beyond pH 9.5, $Co(OH)^{\circ}$ becomes dominant. The activity of Co^{2+} ion in solution decreases 100-fold with an increase of a pH unit, whereas the activity of $Co(OH)^{\circ}_2$ does not change with the pH. These predictions are similar to Baes and Mesmer (1976). If $CoCO_3$ was the solid phase that controlled the solubility, the total cobalt concentration in solution at pH 7 would be approximately 10^{-7}M and approximately 10^{-12}M at pH 9.5.

Experimental Adsorption Results

Spencer and Gieseking (1954) studied cobalt adsorption on and release from Wyoming bentonite and Swygert clay. Cobalt was adsorbed more strongly than calcium. They suggested that cobalt was adsorbed on the clays as monovalent hydroxy-cobaltous ions and as divalent cobaltous ions.

Haney (1957) described a test disposal of TBP (tributyl phosphate) scavenged wastes produced by uranium recovery from the Bismuth Phosphate Process. The Bismuth Phosphate Process recovered only weapons grade plutonium from the irradiated, solubilized fuel elements. Rhodes and Nelson (1957) referred to the same waste as Uranium Recovery Plant Waste and gave a cobalt content of from 4×10^{-5} to 4×10^{-3} $\mu c/cm^3$ of ^{60}Co. Glaciofluviatile soil column studies were undertaken and little ^{60}Co was removed by adsorption on the soil. The ^{60}Co was reported to form a complex ion, probably a cobalticyanide complex, that did not undergo ion exchange reactions with the soil. The presence of nonexchangeable ^{60}Co became a limiting factor in the disposal of some wastes. Sorathesn et al. (1960) reported that ^{60}Co behaved like a colloid at pH 8 to 9, and gave a ^{60}Co Kd value of 23,624 on illite.

Friend (1963) reported that suspended solids in a pond environment took up ^{60}Co rapidly, with suspended illite having the most selectivity for cobalt removal of the clay minerals. Wilding and Rhodes (1963) studied the effects of 100 ppm citrate and EDTA on cobalt equilibrium distribution coefficients with the zeolite clinoptilolite and Well-81 sediments. At pH 6.5, citrate enhanced cobalt adsorption on clinoptilolite, the Kd value being 48 with no treatment and 102 with 100 ppm citrate added. With EDTA addition at pH 6.5, the cobalt Kd value fell from 100 to 1 ml/g. Well-81 sediments adsorbed about the same amounts with and without citrate. At pH 7.7, the cobalt Kd was 30 ml/g with no citrate and 26 ml/g with citrate. At 7.7, the cobalt Kd was 1000 ml/g with no EDTA and 1.2 ml/g with EDTA. Tiller et al. (1963) found no correlation between cobalt adsorption and soil mineralogy. Hawkins (1964) described a process of cobalt removal from waste solutions by scavenging on manganese dioxide precipitate and removal of the remaining cobalt by ion exchange on lignite, soil and the natural zeolite clinoptilolite. Distribution coefficients for cobalt were 56, 800 and 24 ml/g for Idaho soil, lignite and clinoptilolite, respectively.

Gonzalez and Gomez (1961) found that most of the cobalt in Andalusian soils was found in oxide and hydroxide gels associated with clays. There was a positive correlation between cobalt content of the soil and Fe_2O_3 content.

Basu and Mukherjee (1965) obtained cobalt isotherms on montmorillonite clay. Cobalt exchange behavior was very similar to that of potassium, ammonium and nickel cations.

Humic acid was isolated from the A horizon of the Emory silt loam and equilibrated with Co^{+2} and ^{60}Co chloride solutions by Dunigan and Francis (1972). Subsequent salt solution washings of the humic acid removed 91 to 99% of the ^{60}Co.

James and Healy (1972) showed the adsorption isotherm for 1.2×10^{-4} M Co^{+2} on silica at 25°C as a function of pH. Adsorption is 10% at pH 6 and greater than 90% at pH 8. Computed hydrolysis data at this cobalt concentration are also shown.

Tewari et al. (1972) investigated the adsorption of Co^{+2} by Fe_3O_4, Al_2O_3 and MnO_2 as a function of concentration, solution pH and temperature in connection with the transport of cobalt adsorbed on corrosion product oxides. Hydrolysis of Co^{+2} was suggested as a possible mechanism for the marked dependence of cobalt adsorption on pH and temperature.

Migration Results

Field Studies--

Haney (1967) reported the disposition of radioactivity beneath several Hanford ground disposal sites, among them the 216-BY covered trenches. The eight BY trenches were used from December 1954 to December 1955 and received 3.4×10^7 liters of radioactive U-plant, high-salt scavenged waste (0.1$\underline{M}$ PO_4^{3-}, total dissolved solids = 350 g/liter, mostly $NaNO_3$, pH = 9.5, ^{60}Co = 4×10^{-3} to 4×10^{-5} $\mu Ci/cm^3$). The waste contained enough phosphorus (some of it as degraded tributyl phosphate) to complex most of the cobalt in a neutral to anionic species that essentially passed through the soil column without reaction. The groundwater beneath the trenches was contaminated with 1×10^{-5} $\mu Ci/cm^3$ of ^{60}Co. The ^{60}Co on the soil column (68 m to the water table) was uniformly distributed at concentrations of from 1×10^{-5} $\mu Ci/g$ of soil to 1×10^{-4} $\mu Ci/g$ of soil.

Magno et al. (1970) reported that ^{60}Co constituted only <0.1% of the beta activity in surface drainage from the Nuclear Fuel Services plant Lagoon system in western New York State. Even that small amount of ^{60}Co constituted 40% of the ^{60}Co entering the system of lagoons because of the small amount of ^{60}Co disposed to the lagoon. The ^{60}Co in the effluent was relatively small, but was all in solution and thus able to travel with the surface water. The implication is that the "soluble" ^{60}Co was migrating as a complexed species.

Duguid (1976) studied the seepage waters from burial grounds at Oak Ridge used for the disposal of intermediate-level liquid wastes from 1962 to 1965. Trench 7 seepage contained ^{60}Co combined in an organic complex that was not readily adsorbed by the surrounding shale. Groundwater, as well as surface water, contained these readily-transported ^{60}Co complexes.

Laboratory Studies--

The chemical mechanism of ^{60}Co transport in groundwater from intermediate-level liquid waste Trench 7, Oak Ridge, Tennessee, was studied by Means et al. (1976). A small volume groundwater seep 50 m east of Trench 7 contained ^{60}Co in soil concentrations of 10^4 to 10^6 dpm/g and water concentrations of 10^3 dpm/ml. The ^{60}Co was transported as a complex with molecular weight less than 700 according to Sephedex gel G-10 studies. The G-10 is designed to retard the passage of organic solutes with molecular weights less than 700. The implication is that the ^{60}Co is complexed by low molecular weight natural organics. Migration of ^{60}Co would be negligible in the absence of organic complexation because the soil adsorption capacity for inorganic forms of ^{60}Co was reported to be extremely high. Manganese oxides in the Conasauga shale were the principal adsorbents of ionic and weakly complexed ^{60}Co.

Saas and Grauby (1973) studied the migration of cobalt and its transfer mechanisms from nuclear reactor to river water, irrigation water and finally groundwater. Three fractions of ^{60}Co were differentiated including a chelated fraction, an exchangeable fraction and a hydrosoluble fraction. The hydrosoluble fraction was defined as the totality of the organic and mineral components of the soil that are water soluble. The different fractions in a brown, calcareous soil were given. The hydrosoluble fraction constituted about 70%, the exchangeable fraction about 20% and about 10% was chelated from river water containing ^{60}Co. The hydrosoluble form on an alluvial calcareous soil column varied from 10% at the point of input to 60% at 17 cm depth. The water soluble material was only slightly biodegradeable, eventually migrating to the groundwater through application in irrigation water. The pollutants in the river water, including industrial wastes and municipal sewage, are responsible for the rapidly migrating hydrosoluble fraction. The authors suggest that the quality of surface drainage water will have to be taken into account during nuclear reaction siting.

Summary

Among the various soil components, Fe_2O_3 (Gonzalez and Gomez, 1964) and illite (Friend, 1963; Sorathesn et al., 1960) have been shown to have a strong affinity for cobalt. The adsorption of cobalt by soil minerals have been attributed to mainly an ion exchange phenomenon (Hawkins, 1964; Basu and Mukherjee, 1965). With the increase in pH (especially 6 to 9) the adsorption of cobalt increases (James and Healy, 1972; Tewari, Campbell and Lee, 1972). This increase in adsorption with pH has generally been explained as due to the formation of cobalt colloids (Sorathesn et al., 1960) and hydrolysis of Co^{2+} (Tewari et al., 1972). The presence of various complexing ions such as EDTA, cyanide, and fulvic acids have been shown to reduce the adsorption by soil minerals (Wilding and Rhodes, 1963; Rhodes and Nelson, 1957; Dunigan and

Francis, 1972). These laboratory results are consistent with the theoretical predictions (Figure 3-8) which indicate that in acidic pH values cobalt would predominantly exist as Co^{2+} and with the increase in pH it hydrolyzes to $CoOH^+$ and $Co(OH)_2^\circ$.

Discrete cobalt minerals have not been identified in soils. High concentrations of cobalt are required to precipitate cobalt minerals presented in Figure 3-4 under acidic pH values. It is not likely that any of the minerals would exist in the acidic soil environment. However, in highly alkaline conditions, $CoCO_3$ would maintain fairly low concentrations of Co in solution and thus could exist in the soil environment.

Cobalt is apparently relatively easily complexed by natural organics (Duguid, 1976; Means et al., 1976) and by synthetically-produced organics (Haney, 1967; Saas and Grauby, 1973), and as such is able to migrate with relative ease through the soil column with which it would normally react by adsorption.

References

Baes, C. F., Jr. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Basu, A. N. and S. K. Mukherjee. 1965. Interaction Between Montmorillonite Clay and Trace Element Cations. II. Exchange Behavior of Cobalt, Nickel and Chromium Ions in Clays. J. Indian Soc. Soil Sci. 13:251-256.

Chase, M. W., J. L. Curnutt, H. Prophet, R. A. McDonald and A. N. Syverud. 1975. JANAF Thermochemical Tables, 1975 Supplement. Journ. Phys. and Chem. Ref. Data 1974. (1)4.

Duguid, J. O. 1976. Annual Progress Report of Burial Ground Studies at Oak Ridge National Laboratory: Period Ending September 30, 1975. ORNL-5141.

Dunigan, E. P. and C. W. Francis. 1972. Adsorption and Desorption of Cobalt 60, Strontium 85, and Cesium 137 on Soil Humic Acid. Soil Science. 114:494-496.

Friend, A. G. 1963. The Aqueous Behavior of ^{85}Sr, ^{137}Cs, ^{65}Zn, and ^{60}Co as Determined by Laboratory Type Studies. IN: Transport of Radionuclides in Fresh Water Systems. TID-7664.

Gonzalez, G. F. and A. M. Gomez. 1961. Geochemistry of Cobalt in Soils of Western Andalusia. IV. Cobalt Clays and Correlation Between Cobalt and Iron, Clay and Manganese Contents. An. Edafol. Agroboil. 23:563-572.

Hacquaert, A. L. 1925. Pink Calcite from Tantara (Katanga). Natuurw. Tijds. Antwerp, vol. 7, p. 102.

Haney, W. A. 1957. Disposal of High Cobalt-60 Scavenged Wastes. HW-48862.

Haney, W. A. 1967. Final Report on the Effects of Ben Franklin Dam on Hanford. BNWL-412, pp. 8-13.

Hawkins, D. B. 1964. Removal of Cobalt and Chromium by Precipitation and Ion Exchange on Soil, Lignite and Clinoptilolite from Citrate-Containing Radioactive Liquid Waste. IDO-12036.

James, R. O. and T. W. Healy. 1972. Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface. J. Colloid Interfac. Sci. 40:65-81.

Latimer, W. M. 1952. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. Prentice Hall, Inc.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Means, J. L., D. A. Crerar, and J. O. Duguid. 1976. Chemical Mechanisms of ^{60}Co Transport in Ground Water from Intermediate - Level Liquid Waste Trench 7: Progress Report for Period Ending June 30, 1975. ORNL/TM-5348.

Moore, L. R. 1964. The Microbiology, Mineralogy and Genesis of a Tonstein. Prac. Yorkshire Geol. Soc. 34:235-292.

Rhodes, D. W. and J. L. Nelson. 1957. Disposal of Radioactive Liquid Wastes from the Uranium Recovery Plant. HW-54721.

Robie, R. A., and D. R. Waldbaum. 1968. Thermodynamic Properties of Minerals and Related Substances at 298.15°K (25°C) and One Atmosphere (1.013 bars) Pressure and at Higher Temperatures. Geol. Surv. Bull. 1259.

Saas, A. and A. Grauby. 1973. Mechanisms for the Transfer to Cultivated Soils of Radionuclides Discharged by Nuclear Power Stations into the System: River-Irrigated Soil-Ground Water. IN: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/57, pp. 255-269.

Shannon, R. D. and C. T. Prewitt. 1969. Effective Ionic Radii in Oxides and Fluorides. Acta. Cryst., B. 25:925.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Sorathesn, A. G. Bruscia, T. Tamura, and E. G. Struxness. 1960. Mineral and Sediment Affinity for Radionuclides. CF-60-6-93.

Spencer, W. F., and J. E. Gieseking. 1954. Cobalt Adsorption and Release in Cation Exchange Systems. Soil Sci. 78:267-276.

Tewari, P. H., A. B. Campbell, and W. Lee. 1972. Adsorption of Cobalt (+2) by Oxides from Aqueous Solution. Can. J. Chem. 50:1642-1648.

Tiller, K. G., J. F. Hodgson, and M. Peech. 1963. Specific Sorption of Cobalt by Soil Clays. Soil Science. 95:392-399.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultant Bureau.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm. 1968. Selected Values of Chemical Thermodynamic Properties. Tables for the First Thirty-Four Elements in the Standard Order of Arrangement. NBS Technical Note 270-3.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm. 1969. Selected Values of Thermodynamic Properties. Tables for Elements 35 Through 53 in the Standard Order of Arrangement. NBS Technical Note 270-4.

Wilding, M. W. and D. W. Rhodes. 1963. Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho. IDO-14624.

Young, R. S. 1957. The Geochemistry of Cobalt. Geochim. et Cosmochim. Acta. 13:28-41.

CURIUM

Natural Soil and Rock Distributions

The element curium has not been reported to occur naturally in soil or rocks.

Brief Chemistry

Thirteen isotopes of curium are known from ^{238}Cm to ^{250}Cm, most with relatively short half-lives. There are no naturally-occurring curium isotopes.

The curium isotopes can be produced in reactors by n reactions on ^{239}Pu or by decay of californium isotopes (Keller, 1971). The LWR reprocessing waste isotopes are given in Table 3-35. Curium-250 also has a long half-life, but yields are normally very low. Curium can exist in Cm(III) or Cm(IV) oxidation states, but stabilization of Cm(IV) requires high concentrations of fluoride ions to form the anionic complexes CmF_5^- and CmF_6^{-2} (Keller, 1971). Only trivalent curium is normally stable in aqueous solutions. The ionic radius of Cm^{+3} in coordination number 6 is 0.986 Å. Trivalent curium forms many complexes with inorganic ligands found in wastes and in groundwaters.

TABLE 3-35. CURIUM RADIONUCLIDE DATA
(WEAST, 1976)

Isotope	Half-Life	Decay Mode
^{242}Cm	163 days	α
^{243}Cm	32 years	α
^{244}Cm	17.6 years	α
^{245}Cm	9,300 years	α
^{246}Cm	5,500 years	α
^{247}Cm	470,000 years	α

Solid Phase and Solution Equilibria

Curium forms hydride, hydroxide, halides, oxides, and organometallic compounds (Keller, 1971). Except for CmF_3, a search for thermodynamic data for these compounds was unsuccessful. Therefore, predictions regarding the stability of formation of various compounds of curium in soils cannot be made at this time.

Curium is found in two oxidation states [Cm(III) and Cm(IV)] in aqueous solution (Keller, 1971). Curium (IV) is not stable in solutions because of self-radiation and rapid changes to Cm(III). Only trivalent curium is stable in aqueous solutions. Keller (1971) reports that the behavior of Cm^{3+} in solution is similar to lanthanide elements. Most of the lanthanides form trivalent hydroxides in natural waters with solubility products of $<10^{-19}$ (Vickery, 1953). Thomas and Jacobs (1969) found that the activity of curium in 0.1M NaCl solutions which contained approximately 10^{-11} M/l of curium decreased at pH values above 3. They attributed this decrease in activity in pure solutions to either precipitation or adsorption on walls. If this is assumed to be due to precipitation, the solubility product of curium hydroxide would be at least as low as the lanthanides, and probably much lower.

Since thermodynamic data for the curium compounds is not available, it was decided to plot the solution species in equilibrium with $Cm(OH)_3$ with an assumed log K° of Z for the dissolution of $Cm(OH)_3$ [$Cm(OH)_3 + 3H^+ \rightleftarrows Cm^{3+} + 3H_2O$] in order to show the relative activity of various solution species of curium with the changes in pH. Keller (1971) reviewed the curium data and stated that little work has been performed on the complex chemistry of curium and since a wide variation occurs in stability constants determined by various authors, these values should be regarded as relative rather than absolute. The thermodynamic data used to develop Figure 3-9 were obtained from the following sources: Trotman-Dickinson (1973), $CmCl^{2+}$, CmF^{2+}, $CmSO_4{}^+$; Jones and Choppin (1969), $CmNO_3{}^{2+}$; Shalinets and Stepanov (1972), $CmOH^{2+}$, $Cm(OH)_2{}^+$ and Moskin (1969), $CmH_2PO_4{}^{2+}$.

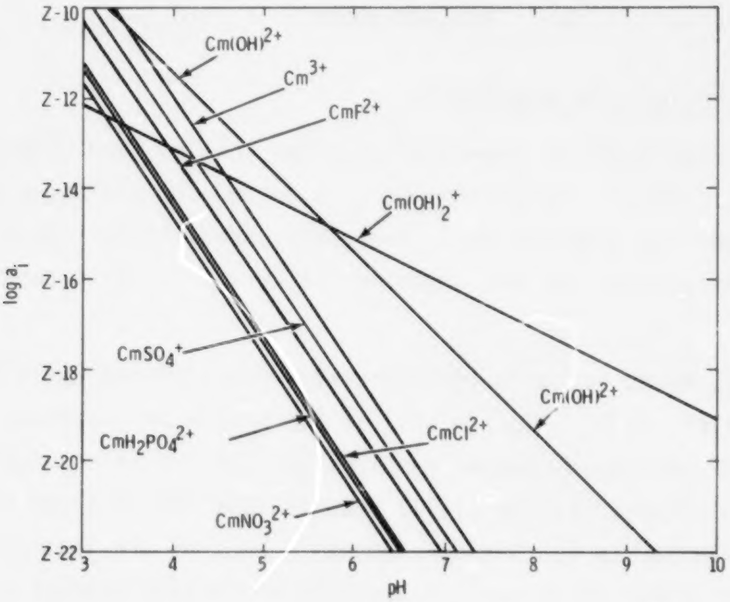

Figure 3-9. The activity of various curium ion species in equilibrium with $Cm(OH)_{3(s)}$ with $pF^- = 4.5$, $pCl^- = pSO_4{}^{2-} = 2.5$, $pNO_3^- = 3.0$ and $pH_2PO_4^- = 5.0$.

It can be seen from Figure 3-9 that curium forms various solution complexes with OH^-, F^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}. The activity of all the complexes decreases with the increase in pH. The solution complexes of PO_4^{3-}, Cl^-, NO_3^-, do not contribute significantly to the total curium concentration in solutions. The most dominant solution species in pH ranges of <3.3, 3.3-5.7, 5.7 and up are Cm^{3+}, $Cm(OH)^{2+}$, and $Cm(OH)_2^+$, respectively.

Experimental Adsorption Results

The adsorption characteristics of ^{242}Cm on several clays was measured in distilled water and 0.1M NaCl by Thomas and Jacobs (1969). Adsorption was not a function of ion exchange capacity because greater adsorption occurred in 0.1M NaCl solutions (Jacobs et al., 1966) than in distilled water solutions. When adsorption studies were made as a function of pH, some curium was removed from solution even without the addition of clay at pH values above 3. This was due to precipitation or to adsorption on glass walls. Addition of clay caused a considerable increase in adsorption possibly because increased surface area was available for deposition. Column loading studies of ^{242}Cm tagged 0.1M NaCl showed normal ion exchange chromatographic breakthrough at pH 1. Above pH 1, the effluent deviated from normal chromatographic curves and remained constant during the entire run. The effluent/influent ^{242}Cm concentration ratio at pH 3 was about 0.008; at pH 7 the ratio was 0.028; and at pH 10 the ratio was 0.150. Although ^{242}Cm precipitated from stock solution at pH values above 3, the column leakage of curium increased with increasing pH. The leakage is probably caused by hydroxy and oxo-complexes forming radiocolloids. Movement of curium through soil is probably restricted by filtration and surface adsorption of radiocolloids rather than by ion exchange.

Sheppard et al. (1976) investigated the distribution values of ^{244}Cm on several Washington and South Carolina soils. The 50 day distribution results for trace ^{244}Cm in a distilled water solution are given in Table 3-36. The distribution for curium between soil and solution increased with time. The distribution values were computed in the same manner as a Kd value. However, Kd values are defined as obtained at soil-solution equilibrium which these values did not attain. The slow increase in distribution values were interpreted by the authors as due to the presence of colloids. It was also shown that iron and manganese oxides were effective scavengers for curium.

TABLE 3-36. CURIUM 50-DAY DISTRIBUTION COMPUTED FROM SHEPPARD ET AL., (1976)

Soil Identity	Distribution, ml/g	Monthly Change in Distribution
Muscatine Silt Loam	1330	+8%
Burbank Loamy Sand	106	+27%
Ritzville Silt Loam	704	+40%
Fuquay Sand 0-5 cm Depth	1850	+26%
Fuquay Sand 5-15 cm Depth	1850	+28%
Fuquay Sand 15-50 cm Depth	1240	+18%

Migration Results

Field Studies--

Duguid (1976) reported that Bondietti had shown that the alpha contamination in water from seep S-4 along the south side of burial ground 5, Oak Ridge, Tennessee, was due to 3.2 x 10^{-7} μCi/ml of ^{244}Cm and 3.2 x 10^{-8} μCi/ml of ^{238}Pu. The burial trenches in burial ground 5 were overflowing because precipitation infiltrated the trenches, reached the less permeable trench bottom and flowed out the lower end of the trench in a seep. The ^{244}Cm and ^{238}Pu were presumably picked up by the water in its passage through the waste-filled burial trench. Bondietti and Reynolds (1977) reported that seepage water, presumably from burial ground 5, contained 700 ± 70 dpm/l of ^{244}Cm in the filtrate from a 0.45 μm filter.

Laboratory Studies--

Nishita et al. (1976) determined the extractability of plutonium and curium from a contaminated soil as a function of pH and soil components. The organic matter and pH influences hydrolysis, precipitation, coprecipitation and adsorption of the radionuclides. In the work, 2 g of soil were suspended in 25 ml of extracting water, in duplicate, and the pH adjusted with NaOH or HNO_3. The Kd values computed from Nishita et al. (1976) are given in Table 3-37 for the untreated Aiken clay loam, a kaolinitic soil, at several pH values. The Aiken clay loam also was treated sequentially with progressive treatments to remove salts, organic matter, carbonates, manganese oxides, ion oxides, free silica and alumina and amorphous aluminosilicates. The organic matter was shown to have the greatest ability to retain curium, but this was a function of pH as well. Below pH 4.5, curium was less strongly adsorbed whether organic matter was present or not.

TABLE 3-37. Kd VALUES FOR ^{242}Cm IN UNTREATED AIKEN CLAY LOAM (NISHITA ET AL., 1976)

pH	^{242}Cm Kd, ml/g	pH	^{242}Cm Kd, ml/g
1.21	85.7 ± 12	8.54	4608 ± 1635
2.12	2,457 ± 6	9.43	1776 ± 142
2.56	6,803 ± 46	10.31	690 ± 38
4.69	100,000 ± 30,000	11.25	358 ± 2.7
5.55	100,000 ± 10,000	12.22	190 ± 3.3
7.08	71,429 ± 10,204	13.25	272 ± 23

Summary

No information is available on possible curium compounds in soils and sediments. It appears that curium precipitation as $Cm(OH)_3$ in alkaline solutions may control curium concentrations in those solutions. Theoretical calculations (Figure 3-9) indicate that Cm^{3+} hydrolyzes even in acidic solutions (pH 3.3 and above). Very little reliable information is available on interactions of curium with soils and sediments, and none on curium interactions with rocks. What little data are available indicate that curium adsorption is not a function of ion exchange capacity of the soil (Thomas and Jacobs, 1969; Jacobs et al., 1966), and that precipitation and/or formation of radiocolloids may predominately influence curium adsorption reactions (Thomas and Jacobs, 1969; Sheppard et al., 1976).

References

Bondietti, E. A. and S. A. Reynolds. 1977. Field and Laboratory Observations on Plutonium Oxidation States. BNWL-2117, pp. 505-538.

Duguid, J. O. 1976. Annual Progress Report of Burial Ground Studies at Oak Ridge National Laboratory: Period Ending September 30, 1975. ORNL-5141.

Jacobs, D. G., Y. E. Kim, and O. M. Sealand. 1966. Application of Mineral Exchange to Reactor Technology. ORNL-4007, pp. 27-33.

Jones, A. D. and G. R. Choppin. 1969. Complexes of Actinide Ions in Aqueous Solutions. Actinide Reviews. 1:311-336.

Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie GmbH.

Moskin, A. I. 1969. Complex Formation of the Actinides with Anions of Acids in Aqueous Solutions. Soviet Radiochemistry. 11:447.

Nishita, H., M. Hmailton and A. J. Steen. 1976. Extractability of ^{238}Pu and ^{242}Cm from a Contaminated Soil as a Function of pH and Certain Soil Components. HNO_3 - NaOH System. Presented at Annual Meeting of Soil Science Society of America, Houston, Texas.

Shalinets, A. B. and A. V. Stepanov. 1972. Investigation of Complex Formation of the Trivalent Actinide and Lanthanide Elements by the Method of Electromigration. XVII. Hydrolysis. Radiokhimiya. 14:280-282.

Sheppard, J. C., J. A. Kittrick, and T. L. Hart. 1976. Determination of Distribution Ratios and Diffusion Coefficients of Neptunium, Americium and Curium in Soil-Aquatic Environments. RLO-2221-T-12-2.

Thomas, W. A. and D. G. Jacobs. 1969. Curium Behavior in Plants and Soil. Soil Science. 108:305-307.

Trotman-Dickinson, A. F. (Executive Ed.). 1973. Comprehensive Inorganic Chemistry. Pergamon Press, New York.

Vickery, R. C. 1953. Chemistry of the Lanthanons. Butterworths Sci. Publ., London.

Weast, R. C., Editor. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio, pp. B349-B350.

EUROPIUM

Natural Soil and Rock Distributions

The europium content of several common rock types are given in Tables 3-38 and 3-39.

TABLE 3-38. EUROPIUM CONTENT OF IGNEOUS ROCKS IN ppm (HASKIN AND SCHMITT, 1967)

Peridotite	Low K Tholeiite	Hawaiian Tholeiite	Andesite	Granodiorite	Leucogranite	Nepheline Syenite
0.2	1.9	1.3	1.0	1.2	0.17	10

TABLE 3-39. EUROPIUM CONTENT OF SEDIMENTARY ROCKS IN ppm (HASKIN ET AL., 1966)

Shale	Quartzite	Limestone	Subgraywacke
2.0	0.09	0.14	1.3

Haskin and Schmitt (1967) gave the value of 2.9 ppm Eu in a composite of 40 North American shales, with a variation in sedimentary rocks of about five times that value.

In a study of rare earths in Russian platform soils, Balashov et al. (1964) reported high europium contents in alkaline soils, the europium precipitating as hydroxide. Acidic soils probably allow complexing and removal of the europium and other rare earths.

Brief Chemistry

Europium occurs in two stable isotopes out of a total of 17 isotopes, ^{151}Eu (47.8%) and ^{153}Eu (52.2%). The radionuclides of interest are given in Table 3-40. The oxidation states of europium are trivalent with radius 0.95 Å and divalent with radius 1.09 Å (Ahrens, 1952). The divalent state is typical of europium occurrence, substituting for Ca^{+2} and K^+ in main stage feldspars (plagioclases, microcline, orthoclase). The potential of the Eu(III)/Eu(II) couple is -0.43 volts (Latimer, 1952).

TABLE 3-40. EUROPIUM RADIONUCLIDE DATA (WEAST, 1976)

Isotope	Half-Life	Decay Mode
^{152}Eu	13.6 years	β^+, EC, β^-
^{154}Eu	8.6 years	β^-
^{155}Eu	1.81 years	β^-
^{156}Eu	15 days	β^-

Europous ions are stable in water solutions at low hydrogen ion concentrations (basic pH), and can be formed from Eu^{+3} by zinc reduction. However, the europium in soil solutions is more apt to be in the trivalent than divalent state.

Solid Phase and Solution Equilibria

Europium forms oxides, hydroxides, and salts with chlorides and sulfates (EuO, Eu_2O_3, Eu_3O_4, $Eu(OH)_3$, $EuCl_3 \cdot 6H_2O$, and $Eu_2(SO_4)_3 \cdot 8H_2O$). Thermodynamic data for these solid phases were used to plot the stability of the minerals (Figure 3-10). It can be seen that, except for the hydroxides [$Eu(OH)_3$], all the other minerals considered are too soluble in environmental pH ranges of interest (pH 4-10). In Figure 3-10, $Eu(OH)_3$, Eu_2O_3, $Eu_2(SO_4)_38H_2O$ are the only solids shown. The thermodynamic data for Eu_2O_3 and $Eu(OH)_3$ were obtained from Shumm et al. (1973), and for $Eu_2(SO_4)_3 \cdot 8H_2O$ were obtained from Latimer (1952). The other solids were too soluble and fall beyond the graph boundaries. Of all the solids considered in Figure 3-10, $Eu(OH)_3$ is the most stable in alkaline environments. The results of Serne and Rai (1976) indicate that kinetics of $Eu(OH)_3$ precipitation is very fast and that $Eu(OH)_3$ is the most likely europium solid to maintain the activity of Eu^{3+} in solution in slightly acidic to alkaline conditions. However, where $Eu(OH)_3$ does not precipitate or the europium concentration is below the $Eu(OH)_3$ solubility line, cation exchange reactions are the probable europium adsorption mechanism.

Europium can exist as Eu^{2+} and Eu^{3+}. However, Eu^{3+} is the only state which is stable in water (Baes and Mesmer, 1976). The activity of various solution species of europium in equilibrium with $Eu(OH)_3$ and at assumed concentrations of various anions commonly found in soils is given in Figure 3-11. The thermodynamic data of all the species except $EuOH^{2+}$ and EuF^{2+} were obtained from Schumm et al. (1973). The data for $EuOH^{2+}$ and EuF^{2+} was obtained from Baes and Mesmer (1976) and Walker and Choppin (1967), respectively.

In a general way the solution complexes of europium in decreasing order of importance can be arranged as follows: $Eu_2P_2O_7^{2+}$, $EuSO_4^{+}$, $Eu(SO_4)_2^{+}$, EuF^{2+}, $EuCl^{2+}$, and $EuNO_3^{2+}$. Under the conditions assumed in Figure 3-11, the predominant solution species in pH ranges of <4.5, 4.5-7.75, 7.5-8.85, and >8.85 will be $EuSO_4^{+}$, $Eu_2P_2O_7^{2+}$, $EuSO_4^{+}$, and $EuOH^{2+}$, respectively. Thus, significant

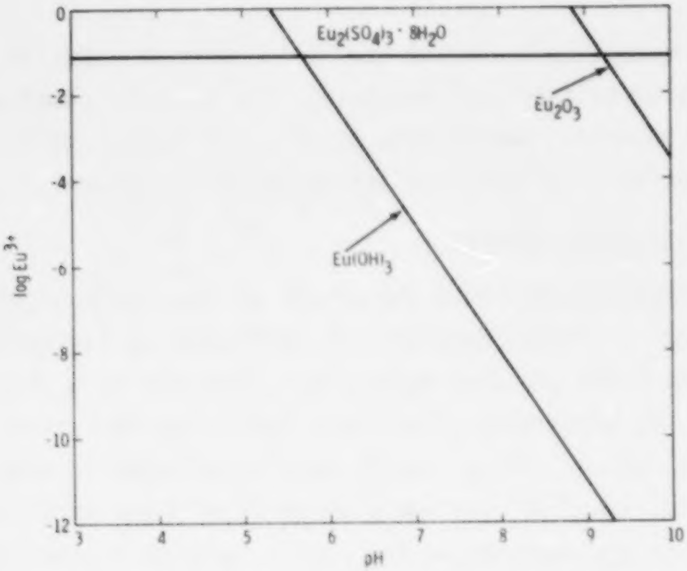

Figure 3-10. The relative stability of various europium solids at $pSO_4^{2-} = 2.5$.

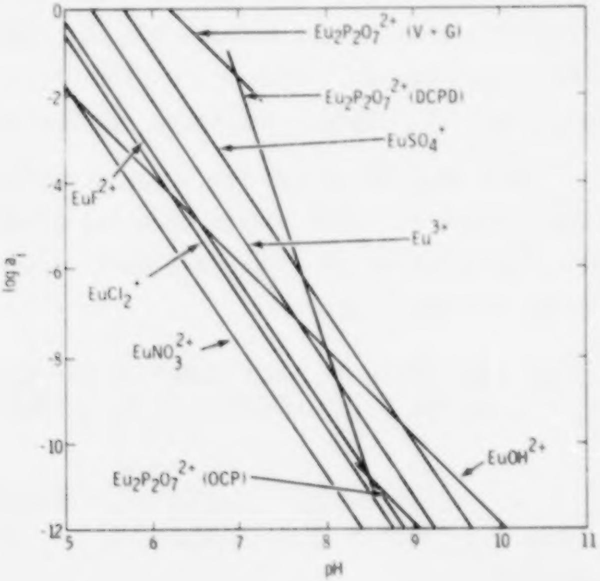

Figure 3-11. The activity of various europium species in equilibrium with $Eu(OH)_3(s)$. Other soil solution conditions included $pSO_4^{2-} = pCl^- = 2.5$, $pNO_3^- = 3.0$, $pF^- = 4.5$ and phosphate levels were from Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP).

quantities of uncomplexed europium (Eu^{3+}) can only be expected in soils with very low levels of sulfate and phosphate. The solution complexes of europium with fluoride, chloride, and nitrate do not contribute significantly to total europium concentration in solution and hence can be ignored.

Experimental Adsorption Results

Bensen (1960) reported that the uptake of rare earths (cerium, promethium and europium) was virtually complete and unaffected by accompanying 0.5M alkali metal and 0.25M alkaline earth metal chlorides at a pH above 7. Below pH 3, however, the adsorption of all rare earths was depressed similarly by the accompanying salts. These results were interpreted to mean that the rare earths, including europium, are ionic at pH below 3 and that they are taken up principally by ion exchange on the soil. Above pH 7, they are precipitated. The rare earths, including europium, appear to exist as tripositive ions.

Baetsle and Dejonghe (1962) gave a europium Kd range in Mol soil (mostly quartz sand) at pH 7.7 as 228 to 705, and reported that at pH >3, europium hydrolyzed. Therefore, above pH 3, the authors did not consider that adsorption was an ion exchange phenomenon. However, a plot of pH versus log Eu activity (Figure 3-11) does not support the above conclusion.

Baetsle et al. (1964) gave Kd values for trace europium in three different waters. The compositions of these waters were not given. Kd results are shown in Table 3-41. The europium Kd values are much larger than the cesium and strontium Kd values for the same soils.

TABLE 3-41. VARIATION OF TRACE EUROPIUM Kd VALUES ON MOL SOILS (BAETSLE ET AL., 1964)

Soil Type	Kd, ml/g Deionized Water, pH 3	Tap Water, pH 7.7	Groundwater, pH 3
Eolian Sand			
Horizon A	214-244	705	130-380
Horizon B	61-75	430	--
Horizon C	69-89	384	--
Mol White Sand	--	801	165-315
Mol Lignitic Sand	--	--	27-1830

Serne and Rai (1976) studied the adsorption-precipitation behavior of europium in soils and pure solutions. The pH of the various europium solutions (0.15M $CaCl_2$ plus trace to 50 mg Eu/l) was increased in 0.05 pH increments until precipitation was observed by the Tyndall Beam method. At the point of $Eu(OH)_3$ precipitation, the europium activity and pH was determined. The results are plotted in Figure 3-12 along with the theoretical $Eu(OH)_3$ solubility line. The results indicate that:

1) the kinetics of precipitation of $Eu(OH)_3$ is rapid,
2) the laboratory results agree well with the theoretical $Eu(OH)_3$ solubility,
3) Eu^{3+} does not appear to hydrolyze appreciably because total europium activity in equilibrium with $Eu(OH)_3$ is similar to the calculated Eu^{3+} activity, and
4) for meaningful Kd values, the theoretical solubility of $Eu(OH)_3$ should not be exceeded.

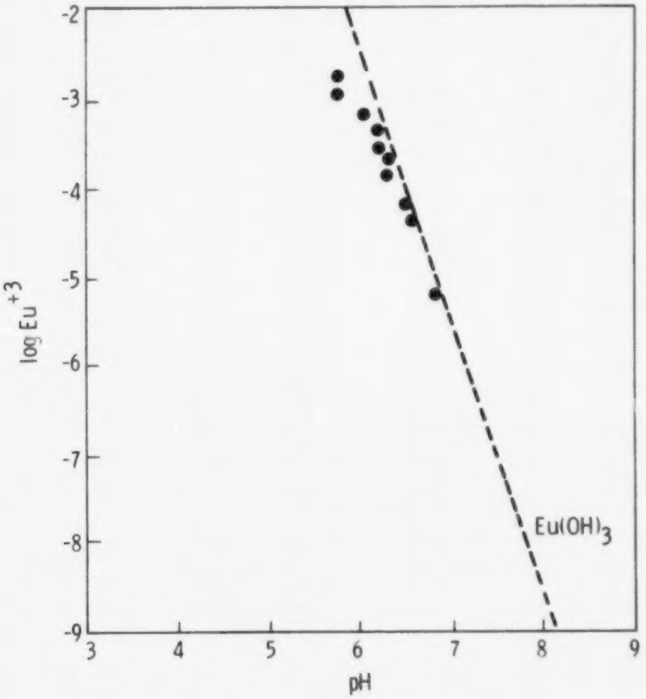

Figure 3-12. The influence of pH on the activity of europium in solution (Serne and Rai, 1976)

Europium adsorption experiments where $Eu(OH)_3$ did not precipitate were conducted, as shown in Table 3-42. The results show that the europium Kd increases with an increase in pH and decreases with increasing europium concentration, below the point of $Eu(OH)_3$ precipitation. These reactions suggest that ion exchange is an active mechanism below the point of $Eu(OH)_3$ precipitation.

TABLE 3-42. EFFECT OF pH AND EUROPIUM CONCENTRATION ON EUROPIUM Kd BY BURBANK SAND*
(SERNE AND RAI, 1976)

Eu, ppm**	Final pH	Kd, mg/l	Eu, ppm**	Final pH	Kd, mg/l	Eu, ppm**	Final pH	Kd, mg/l
0	4.82	46	0.05	5.25	73	5.0	5.20	17.7
0	4.82	48	0.05	5.30	83	5.0	5.20	15.9
0	4.90	51	0.05	5.30	82	5.0	5.25	17.0
0	5.00	75	0.05	5.30	84	5.0	5.32	20.0
0	5.05	70	0.05	5.35	98	50.0	4.70	6.9
0	5.05	69	0.5	4.75	28	50.0	4.70	6.9
0	5.08	75	0.5	4.80	26	50.0	4.73	6.5
0	5.10	84	0.5	4.80	27	50.0	4.88	5.8
0	5.10	78	0.5	5.00	35	50.0	4.90	5.8
0	5.10	78	0.5	5.05	35	50.0	4.90	5.9
0	5.10	82	0.5	5.05	41	50.0	4.90	6.3
0	5.10	75	0.5	5.10	42	50.0	4.90	6.2
0	5.15	93	0.5	5.10	41	50.0	4.90	6.2
0	5.15	90	0.5	5.10	42	50.0	5.00	7.2
0	5.15	81	0.5	5.15	43	50.0	5.00	7.0
0	5.15	93	0.5	5.15	45	50.0	5.00	7.1
0	5.20	94	0.5	5.20	53	50.0	5.15	8.2
0	5.20	98	0.5	5.20	48	50.0	5.15	8.2
0	5.20	98	0.5	5.20	45	50.0	5.20	7.9
0	5.25	107	0.5	5.25	48			
0	5.30	106	0.5	5.25	57			
0	5.30	97	0.5	5.30	54			
0	5.50	153	0.5	5.35	60			
0.05	4.75	32	5.0	4.80	12.4			
0.05	4.75	38	5.0	4.80	11.3			
0.05	4.80	38	5.0	4.80	12.4			
0.05	5.00	63	5.0	4.95	16.9			
0.05	5.00	53	5.0	5.00	18.4			
0.05	5.00	53	5.0	5.05	15.7			
0.05	5.08	56	5.0	5.05	14.8			
0.05	5.08	62	5.0	5.10	15.9			
0.05	5.10	67	5.0	5.10	18.7			
0.05	5.25	71	5.0	5.15	16.4			

---

* One gram samples free of $CaCO_3$ and soluble salts were used

** Various concentrations of Eu were added to 0.15M $CaCl_2$ solutions spiked with Eu^{152}. Samples were equilibrated first for 48 hr and then for 24 hr after adjusting the pH.

Migration Results

Field Studies--

Brookins (1976) reported that europium was retained in the shale that enclosed the fossil nuclear reactor zones at the Oklo mine in Gabon along with the other rare earths produced there by the nuclear reactions 1.8 billion years ago.

Laboratory Studies--

Baetsle et al. (1964) determined the K values associated with europium movement in relation to groundwater movement is given in Table 3-43. These data also may be compared to strontium and cesium K values for the same Mol soils. The europium K values are very pH-sensitive, as the data of Figure 3-12 indicate.

TABLE 3-43. K VALUES OF EUROPIUM IN THE SATURATED SUBSOILS AT MOL, BELGIUM (BAETSLE ET AL., 1964) K IS DEFINED ON PAGE 2-30.

Soil Type	K pH 4	 pH 3
Mol Sand	100	58
Perturbed Profile	1963	511
Mol Sand & Eolian Sand	--	280
Mol Sand & Lignite	--	997
Mol Sand	2472	225
Mol Sand	640	139
Mol Sand	1282	78
Mol Sand	10600	74
Mol Sand	2145	53
Mol Sand	697	64

Mol sand is nearly pure quartz.

Summary

No information on possible europium compounds in soils and sediments is available. Serne and Rai (1976) have shown that the kinetics of precipitation of $Eu(OH)_3$ from pure solutions is rapid. The concentration of europium in equilibrium with $Eu(OH)_3$ decreases 1000-fold with an increase of one pH unit. The activity of europium in equilibrium with $Eu(OH)_3$ is low under highly alkaline conditions and $Eu(OH)_3$ may control europium concentration in alkaline soils and sediments.

Bensen (1960) and Baetsle and Dejonghe (1962) reported that europium appears to be taken up principally by ion exchange below pH 3. Baetsle and Dejonghe (1962) suggested that ion exchange was not the adsorption mechanism above pH 3 because of europium hydrolysis. However, data presented in Figure 3-11 and the results of Serne and Rai (1976) are at variance with the above conclusion. Serne and Rai (1976) have shown that for meaningful determination of Kd values in soils, one must be below the solubility line of $Eu(OH)_3$. Their results, thus obtained, showed that between pH 4.7 and 5.5 the Kd decreases with an increase in pH and Kd decreases as europium concentration increases, which suggests an ion exchange as an adsorption mechanism.

References

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Baes, C. F., Jr. and R. E. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Baetsle, L. and P. Dejonghe. 1962. Investigations on the Movement of Radioactive Substances in the Ground. Part III: Practical Aspects of the Program and Physiocochemical Considerations. IN: Ground Disposal of Radioactive Wastes. TID-7628, pp. 198-210.

Baetsle, L. H., P. Dejonghe, W. Maes, E. S. Simpson, J. Souffriau, and P. Staner. 1964. Underground Radionculide Movement. EURAEC-703.

Balashov, U. A., et al. 1964. The Effects of Climate and Facies Environment on the Fractionation of the Rare Earths During Sedimentation. Geochemistry International. 10:951-969.

Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Haskin, L. A. and R. A. Schmitt. 1967. Rare-Earth Distributions. IN: Researches in Geochemistry. Vol. 2. P. H. Abelson (ed.). John Wiley & Sons, Inc. pp. 234-259.

Haskin, L. A., et al. 1966. Meteoric, Solar, and Terrestrial Rare Earth Distributions. IN: Physics and Chemistry of the Earth. L. H. Ahrens et al. (eds.) Vol. 7. Oxford, Pergamon Press.

Latimer, W. M. 1952. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. Prentice-Hall, Inc.

Serne, R. J. and Dhanpat Rai. 1976. Adsorption-Precipitation Behavior of Eu in Soils and Standard Clays. Agronomy Abstracts. p. 132.

Schumm, R. H., D. D. Wagman, S. M. Bailey, W. H. Evans, and V. B. Parker. 1973. Selected Values of Chemical Thermodynamic Properties. Tables for the Lanthanide (Rare Earth) Elements (Elements 62 through 76) in the Standard Order of Arrangement. NBS Technical Note 270-7. Schwille, F., W. Lippok and D. Weisflog. 1967. Model Experiments on Fluid Flow in the Transition Zone from Unsaturated to Saturated Soil. IAEA-SM-93/11, pp. 151-159.

Walker, J. B., and G. R. Choppin. 1967. Thermodynamic Parameters of Fluoride Complexes of the Lanthanides. Advances in Chemistry Series No. 71. The American Chemical Society, Washington D.C. pp. 127-140.

Weast, R. C., Editor. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio, p. B313.

IODINE

Natural Soil and Rock Distributions

The iodine content of volcanic rocks is given in Table 3-44. Yoshida et al. (1971) tried leaching the iodine from volcanic rocks, and usually removed less than 20% of the total iodine in the rock. The average I value for igneous rocks probably falls within the range of 75 to 150 ppb. Nearly the same average value also would be applicable to metamorphic rocks.

TABLE 3-44. IODINE CONCENTRATION IN VOLCANIC ROCKS

Rock Type	I, ppb	Reference
Basalt (BCR-1) Columbia River, WA	160	Becker and Manuel, 1972
Basalts, Japan, 15	29-140	Yoshida et al, 1971
Andesites, Japan, 10	22-260	Yoshida et al., 1971
Andesite (AVG-1) Guano Valley, OR	270	Becker and Manuel, 1972
Dacites, Japan, 3	43-220	Yoshida et al., 1971
Rhyolite, Japan, 2	26-320	Yoshida et al., 1971
Obsidians, Japan, 3	20-65	Yoshida et al., 1971
Obsidian, Oregon	730	Becker and Manuel, 1972
Obsidian, Arizona	730	Becker and Manuel, 1972
Obsidian, Utah	540	Becker and Manuel, 1972
Obsidian, Mexico	1900	Becker and Manuel, 1972

The abundance of iodine in sedimentary rocks is shown in Table 3-45. Note that the units have changed from ppb in igneous rocks to ppm in sedimentary rocks. Pre-1960 iodine analytical values may have been as much as 35 times too high (Brehler and Fuge, 1974).

While the iodine content of marine sediments depends on the carbon to a large extent, marine sediments are much richer in iodine than sedimentary rocks. Walters and Winchester (1971) examined iodine binding in dry marine sediments and found that most of the iodine was surface-adsorbed or covalent bonded to carbon. About 23% could be extracted with organic solvents.

There is a marked increase in the soil iodine content compared to the rocks they are derived from. For example, the average iodine content of soils was noted as 5 ppm by Vinogradov (1959), who also suggested that much of the soil iodine is atmospherically derived.

TABLE 3-45. IODINE IN SEDIMENTARY ROCKS

Sedimentary Rock	I, ppm	Reference
Sandstones, 11, Bashkiria, USSR	0.5-1.5	Itkina and Lygalova, 1964
Sandstone, white, Klondyke, MO	0.068	Becker et al., 1972
Sandstone, red, Potsdam, NY	0.14	Becker et al., 1972
Argillaceous Sandstone, Portageville, NY	37.6	Becker et al., 1972
Argillaceous Shale, Rochester, NY	13.0	Becker et al., 1972
Calcareous Shale, Lima, NY	38.0	Becker et al., 1972
Limestones, 6, Paleozoic, OK	4.2	Collins et al., 1971
Sediments, SW Barents Sea	405	Price et al., 1970

Many of the iodine studies have noted the correlation of iodine content and humus in the soil (Sinitskaya, 1969; Irinevich et al., 1970; Pennington and Lishman, 1971). De et al. (1971) contacted soils and soil clays with iodide solutions at 20°, 30° and 40°C containing 0.127 g I^-/l, 0.635 g I^-/l and 1.269 g I^-/l. Only the clay minerals showed iodide uptake, with illite adsorbing more iodide than kaolinite or montmorillonite.

Brief Chemistry

There are 24 known isotopes of iodine with 18 of these isotopes having half-lives of less than 1 day. The only stable isotope is ^{127}I. Only ^{129}I, with a half-life of 1.7 x 10^7 years is of long-term interest in high-level waste disposal. The fission product ^{131}I with a half-life of 8.07 days, and ^{125}I with a half-life of 60 days, are often a short-term disposal hazard because of their anionic character and resulting lack of soil adsorption.

Although iodine is known in the (-I), (I), (III), (V) and (VII) oxidation states, its usual occurrence is as the (-I) (iodide) state in fresh waters with a radius of 2.20 Å (Goldschmidt et al., 1926) and as iodate-iodine in marine or similar aqueous environments (Sugawara and Terada, 1958). I^- tends to be a dispersed element in many environments as a result of its large size in comparison with fluorine, chlorine, bromine and hydroxyl ions. Oxidation of iodide ions to produce the iodate ion (IO_3^-) is easily accomplished in basic solution by the reaction: $3I_2 + 6OH^- \rightarrow 5I^- + IO_3^- + 3H_2O$ (Cotton and Wilkinson, 1962). Iodine can form complexes with metal ions, but these are generally the least stable of all the halide complexes, with a few exceptions. Iodine also is a volatile element, subliming at atmospheric pressures without melting.

Examples of iodine minerals include marshite (CuI), iodargyrite (AgI) and coccinite (HgI_2), bellingerite [$Cu(IO_3)_2$], salesite [$CuIO_3(OH)$] and lautarite [$Ca(IO_3)_2$] (Fleischer, 1966). Most such iodine minerals are confined to unusual environments such as the Chilean nitrate deposits.

Solid Phase and Soil Solution Equilibria

Most of the compounds of iodine are very soluble. Some of the insoluble or sparingly soluble compounds include the iodides of Pb and Pd, the hypoiodites of Ag and Hg, and Ba periodates (Pourbaix, 1966). In normal soils the concentration of most of these elements (Pb, Pd, As, Hg and Ba) that iodine forms compounds with is very low. Therefore, they would not be expected to be present in soils.

Iodine can exist in (-I), (I), (III), (V) and (VII) oxidation states. Out of all of these oxidation states, (-I) (I^-, iodide) is the most important and its domain of predominance extends all along the pH scale, almost completely covering a large part of the stability domain of water (Pourbaix, 1966). Thus, it is not surprising that iodine in aqueous solutions free from oxidizing agents generally exists as iodide.

Experimental Adsorption Results

Raja and Babcock (1961) examined the behavior of ^{131}I with two California soils, kaolinite and bentonite. Results of pretreatment by autoclaving, peroxide oxidation, alcohol digestion and extraction of ^{131}I with various salt solutions indicated that the bulk of the iodide retained by soils was due to reaction with organic matter.

Goldberg et al. (1962) determined iodide adsorption on Rainier tuff ground to 100 to 200 mesh from simulated groundwater. The value obtained using ^{131}I was 1.10 ml/g.

Kepak (1965, 1966) studied the sorption of ^{131}I on hydrated aluminum and ferric oxide. One wt% silver oxide was added to the ferric oxide adsorbent. The adsorbent of ferric oxide was 0.06 to 0.1 mm in grain size and the influent solution contained 0.1M $NaNO_3$ at pH 6.9. Slow column breakthrough of the ^{131}I began immediately even from a ^{131}I-distilled water solution. Sixty-six free column volumes (void fraction = 0.66) were loaded to 1% column breakthrough and 758 free column volumes to 90% ^{131}I breakthrough.

The most extensive study of iodine retention by soils was made by Wildung et al. (1975). Iodine was applied to the soils as iodide (I^-) and methyl iodide (CH_3I), a colorless transparent liquid when fresh, with one part soluble in 50 parts of water. The solution normally remained nonionic during the distribution studies. Twenty-two soil types were collected for use in the study in Oregon, Washington and Minnesota with a range of properties as listed in Table 3-46. The $^{131}I^-$ and $CH_3{}^{131}I$ were used in trace quantities in 0.01M $CaCl_2$ solution.

TABLE 3-46. RANGE OF SURFACE SOIL PROPERTIES USED IN THE METHYL IODIDE AND IODIDE ADSORPTIONS (WILDUNG ET AL., 1975)

Cation Exchange Capacity, meq/100 g	Soil Paste pH	Contents, wt%				
		Carbonate	Organic Carbon	Sand	Silt	Clay
5.5 - 90.0	3.6 - 8.9	0 - 6.5	0.23-28.8	14.1-73.1	17.6-58.0	38-46.6

The equilibrium distribution coefficients were treated statistically (Table 3-47). Methyl iodide retention by soils was largely a function of organic carbon and clay content, while iodide adsorption was a partial function of silt content. The mechanisms and causal relationship between the silt and iodide were under further study but were not covered in the report. The mechanisms underlying the cation exchange capacity-methyl iodide relationship are difficult to envision. Regression equations were listed to obtain iodide and methyl iodide Kd values over the soil parameter ranges studied.

Migration Results

Field Studies--

Brown (1967), in the study of groundwater beneath disposal sites at Hanford, mentioned the presence of ^{125}I in the groundwater. The groundwater samples were taken from monitoring wells and the ^{125}I concentration were all less than 2×10^{-5} μCi/ml.

TABLE 3-47. Kd VALUES AND CORRELATIONS RELATING SOIL PROPERTIES IODIDE AND METHYL IODIDE ADSORPTION (WILDUNG ET AL., 1975)

Independent Soil Variables	Correlation Coefficients of Independent and Dependent (Kd) Variables	
	Iodide	Methyl Iodide
Silt wt	0.47*	0.21
Clay wt	0.22	0.43*
Organic Carbon wt	0.06	0.85**
Cation Exchange Capacity	0.21	0.79**
pH	-0.05	-0.41*

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[*] Statistically significant at the 5% confidence level

[**] Statistically significant at the 1% confidence level

Laboratory Studies--

Jacobs (1965) studied the desorption of radioiodine from clays. The clays and Clinch River (Oak Ridge) floodplain sediment were contaminated with iodine vapor from the oxidation of ^{131}I-tagged KI. Desorption studies indicated that the adsorption iodine was in the form of a mixture of HI, I_2 and adsorbed iodine. The rate of desorption decreased with decreased surface concentration, and after 24 hr, the iodine remaining was proportional to the reciprocal of the absolute air temperature. Desorption occurs most rapidly in high humidity air. Most of the iodine was readily removed with tap water. After ten 25 ml increments of Oak Ridge tap water through a 10 g, iodine contaminated Clinch River floodplain sediment, less than 5% of the iodine remained on the sediment. However, removal from 10% to 5% required 60% of the water leach volume, indicating that part of the iodine is relatively tightly held. Some preliminary work with methyl iodide suggested that this chemical form of iodine would move readily through the ground without being adsorbed.

Summary

Because the anion exchange capacities of most soils are minimal over a normal pH range of 6 to 8, the adsorption of iodide (I^-), iodate (IO_3^-) and organic-iodine molecules is normally also minimal (Wildung et al., 1975). However, with soils of low pH (4 to 6), the iodide Kd value can rise to

50 ml/g. Wildung et al. (1975) reported no statistical correlation between organic content and iodide Kd, as they did for methyl iodide. The range of methyl iodide Kd values was from 0.1 to 3.1, much lower than the iodide ion Kd range, even though the correlation between methyl iodide Kd values and soil organic content was statistically significant. Others (Sinitskaya, 1969; Irinevich et al., 1970; Pennington and Lishman, 1971) have shown a positive correlation between iodine content and organic material in the soil where the iodine is apparently covalently bonded to carbon (Walters and Winchester, 1971). It should be kept in mind that iodine, especially when present as an organic-iodine molecule, can change to a vapor phase and migrate much more rapidly than in an aqueous phase.

References

Becker, V. J., J. H. Bennett, and O. K. Manuel. 1972. Iodine and Uranium in Sedimentary Rocks. Chem. Geol. 9:133.

Becker, V. J. and O. K. Manuel. 1972. Chlorine, Bromine, Iodine, and Uranium in Tektites, Obsidians and Impact Glasses. J. Geophys. Res. 77:6353.

Brehler, B. and R. Fuge. 1974. Iodine. IN: Handbook of Geochemistry, Vol. II/3, Springer-Verlag, New York. p. 53-1.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Collins, A. G., J. H. Bennett, and O. K. Manuel. 1971. Iodine and Algae in Sedimentary Rocks Associated with Iodine-Rich Brines. Bull. Geol. Soc. Am. 82:2607.

Cotton, F. A. and G. Wilkinson. 1962. Advanced Inorganic Chemistry. Interscience Publishers.

De, S. K., S. S. Rao, C. M. Tripathi, and C. Rai. 1971. Retention of Iodide by Soil Clays. Indian Journal of Agricultural Chemistry. 4:43-49.

Fleischer, M. 1966. Index of New Mineral Names, Discredited Minerals and Changes of Mineralogical Nomenclature in Vols. 1-50 of the American Mineralogist. Am. Mineral. 51:1248.

Goldberg, M. C., V. J. Janzer, C. G. Angelo, and W. A. Beetem. 1962. The Effect of Sodium Ion Concentration on Distribution Coefficients for Tuffs from NTS. U.S.G.S. Technical Letter NTS-16.

Goldschmidt, V. M., T. Barth, G. Lunde, and U. W. Zachariasen. 1926. Geochemische Verteilungsgesetze der Elemente. VII. Skrifter Norske Videnskaps-Akad. Oslo, I. Mat-Naturv. Kl., No. 2.

Irinevich, A. D., I. Z. Rabinovich, and V. A. Fil'Kov. 1970. Iodine in Moldavian Soils. Pochvovedenie. 58.

Itkina, E. S. and V. W. Lygalova. 1964. Geochemistry of Iodine and Bromine in the Carboniferous Horizon and in the Domanik and Bavly Formations of Some Petroliferous Areas of Bashikiria. IN: The Geochemistry of Oil and Oil Deposits. L. A. Gulyayeva (ed.). Israel Program for Scientific Translations.

Jacobs, D. G. 1965. Desorption of Radioiodine from Clays. ORNL-P-1581.

Kepak, F. 1965. Sorption of Small Amounts of Radioiodine as Iodide Anions on Hydrated Ferric Oxide Containing Silver. Collection Csechoslov. Chem. Commun. 31:1493-1500.

Kepak, F. 1966. Sorption of the Radioisotopes ^{35}S, ^{131}I, and ^{106}Ru on Hydrated Oxides in Laboratory Columns. Collection Czechoslov. Chem. Commun. 31:3500-3511.

Pennington, W. and J. P. Lishman. 1971. Iodine in Lake Sediments in Northern England and Scotland. Biol. Rev. 46:279-313.

Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, England.

Price, N. B., S. E. Calvert, and P. G. W. Jones. 1970. The Distribution of Iodine and Bromine in the Sediments of the Southwestern Barents Sea. J. Marine Res. 28:22.

Raja, M. E. and K. L. Babcock. 1961. On the Soil Chemistry of Radioiodide Soil Science. 91:1-5.

Sinitskaya, G. I. 1969. Iodine Content of the Zeya-Bureya Plain Soils. Uch. Zap. Dal'nevost. Gos. Univ. 27:72.

Sugawara, K. and K. Terada. 1958. Oxidized Iodine in Sea Water. Nature. 182:250.

Vivogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.

Walters, L. J. and J. W. Winchester. 1971. Neutron Activation Analysis of Sediments for Halogens Using Szilard-Chalmers Reactions. Anal. Chem. 43:1020.

Wildung, R. E., R. C. Routson, R. J. Serne, and T. R. Garland. 1975. Pertechnetate, Iodide and Methyl Iodide Retention by Surface Soils. BNWL-1950. Pt. 2. pp. 37-40.

Yoshida, M., K. Takahashi, N. Yonehara, T. Ozawa, and I. Iwasaki. 1971. The Fluorine, Chlorine, Bromine and Iodine Contents of Volcanic Rocks in Japan. Bull. Chem. Soc. Japan. 44:1844.

NEPTUNIUM

Natural Soil and Rock Distributions

Very small quantities of ^{237}Np ($^{237}Np/^{238}U = 10^{-12}$) were reported by Keller (1971) but for practical purposes neptunium does not occur naturally in soils or rocks.

Brief Chemistry

There are 16 known isotopes of neptunium from ^{228}Np to ^{241}Np (Keller, 1971). Only ^{237}Np, a neutron reactor product of ^{238}U (n,2n) and ^{235}U $(n,\gamma)^2$, with a half-life of 2.14 x 10^6 years and ^{239}Np (2.35 days) are of interest. The >5000 year half-life ^{236}Np is a cyclotron product only while the 22-hr half-life ^{236}Np yields ^{236}Pu as a daughter. Neptunium exists in aqueous solutions in five oxidation states, Np(III), Np(IV), Np(V), Np(VI) and Np(VII). In the absence of complexing agents, the first four oxidation states exist as hydrated ions $Np^{+3} \cdot aq$, $Np^{+4} \cdot aq$, $NpO_2^+ \cdot aq$ and $NpO_2^{+2} \cdot aq$ (Keller, 1971). Np(VII) is a strong oxidizing agent that is stable in strong alkaline solutions as NpO_5^{-3}. The most stable oxidation state in solution is the pentavalent one where neptunium exists as a single charged neptunyl ion, $NpO_2^+ \cdot aq$, with symmetrical linear bonding $(O\text{-}Np\text{-}O)^+$. It hydrolyzes only at a pH of greater than 7, disproportionates only at high acid concentrations and forms no polynuclear complexes (Keller, 1971). The NpO_2^+ ion is a poor complexing agent with inorganic ligands.

Solid Phase and Solution Equilibria

The thermodynamic data are lacking for neptunium compounds other than oxide and hydroxides (Burney and Harbour, 1974). Figure 3-13 relates the activity of NpO_2^+ to pH under an oxidizing environment (pO_2 0.68) in equilibrium with neptunium oxide and hydroxides. Since Figure 3-13 was made using Np(V) (NpO_2^+) as the y axis, the solubility of Np(IV) minerals would decrease and Np(VI) minerals would increase with an increase in reducing conditions. In an oxidizing environment [$pO_{2(g)} = 0.68$ atm] the solids in an increasing order of stability are $Np(OH)_4$, NpO_2, NpO_2OH, $NpO_2(OH)_2$. Under the oxidation-reduction conditions represented by $pO_{2(g)} > 3.8$ atm, NpO_2 would be the most stable compound. Since NpO_2 maintains very high concentrations of neptunium in solution, especially in acidic and very oxidizing environments, it is unlikely that NpO_2 would be found as a discrete solid in such terrestrial environments. It may exist in very reducing conditions.

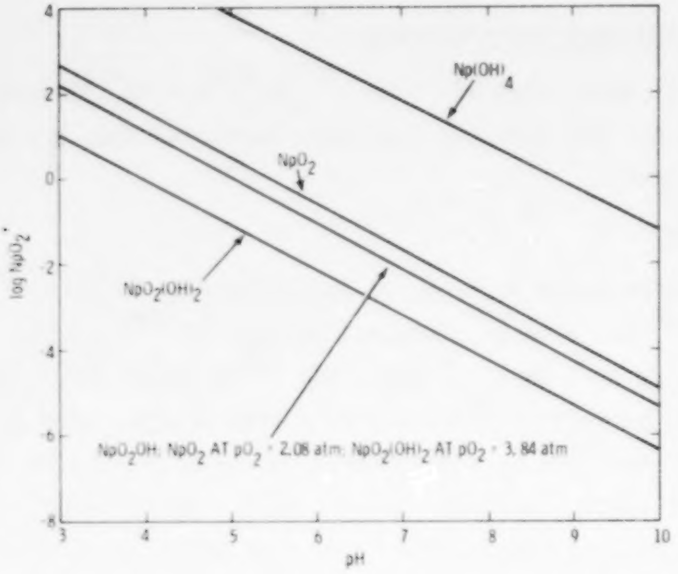

Figure 3-13. The relative stability of various neptunium solids in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm]

The activity of various solution complexes of neptunium in equilibrium with $NpO_2(s)$ in an oxidizing environment (pO_2 = 0.68) and assumed weathering environment is given in Figure 3-14. Thermodynamic data for $NpO_2\ HPO_4^-$ were obtained from Sillen and Martell (1964). The remaining data were from Burney and Harbour (1974). The solution complexes of Np(IV), Np(V), and Np(VI) in order of increasing importance are Np(IV), Np(VI), and Np(V). The activity of Np(IV) and Np(VI) complexes is so small that these complexes can be safely ignored since they would not contribute significantly to the total activity of Np in solution (Burney and Harbour, 1974). The lines of Np(V) and Np(VI) complexes will shift downward with the increase in reducing environment but still be parallel to the present lines. Under the conditions assumed in Figure 3-14, NpO_2^+ is the most dominant solution species in a pH range of 0 to approximately 9. Beyond pH 9, $NpO_2HPO_4^-$ and $NpO_2HCO°_3$ would control the total concentration of neptunium in solution.

NpO_2^+ is the usual form of charged neptunium species up to pH 9. Above pH 9, an uncharged bicarbonate complex is formed. According to Keller (1971) neptunium (V) does not hydrolyze below a pH of 7. Hence, a singly charged

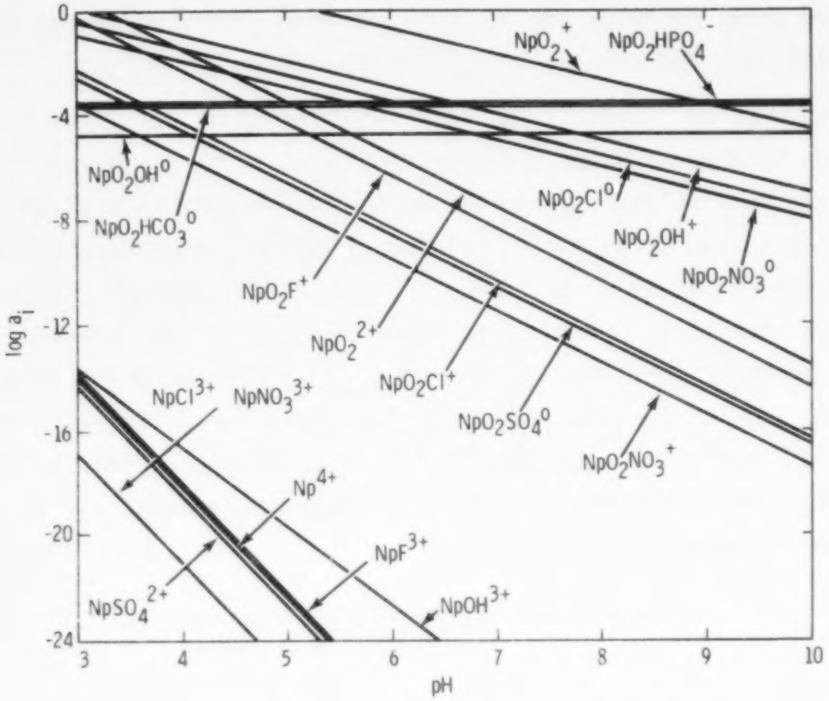

Figure 3-14. The activity of various neptunium species in equilibrium with $NpO_2(s)$ in an oxidizing soil environment $[pO_2(g) = 0.68 \text{ atm}]$, $pCl^- = pSO_4{}^{2-} = 2.5$, $pHO_3{}^- = 3.0$, $pF^- = 4.5$ and $pH_2PO_4{}^- = 5.0$.

neptunyl ion is the usual form. Hence, NpO_2^+ would be expected to enter into ion exchange reactions. NpO_2^+ does not compete favorably with Ca^{+2} and other common divalent ions, and the distribution coefficients are usually relatively low on most soils (Routson et al., 1976; Sheppard et al., 1976).

Experimental Adsorption Results

Bensen (1961) examined the adsorption on minerals of radionuclides in reactor effluent cooling water. One of the radionuclides studied was ^{237}Np, which was adsorbed on 25 different common sulfide, silicate and carbonate minerals, 0.05 to 0.25 mm, in equilibrium tests with trace amounts in Columbia River water at 80°C. According to Bensen, neptunium was adsorbed poorly or not at all by the minerals tested.

Robertson (1974) determined the speciation of neptunium in the cooling water effluent from the Hanford N reactor. Through the use of filter membranes and cation and anion exchange resins, the following distribution was observed: 26% particulate, 70% cationic, <3% anionic and <1% non-ionic.

Routson et al. (1975, 1976) determined neptunium Kd values for a Washington sand and a South Carolina sandy clay. The properties of these soils are given in Table 3-48. The neptunium Kd values are given in Table 3-49. Pre-equilibrations of the soils with nonradioactive solutions prior to contact with the traced solution containing ^{237}Np were carried out. Calcium nitrate and sodium nitrate salts were used as calcium and sodium ion sources. Cation exchange of NpO_2^+ cannot be the principal adsorption mechanism because Na^+ concentration essentially does not affect the neptunium Kd values from no sodium competition to 3.0M Na^+ competition. Calcium has some affect on the neptunium Kd, but much less than there would be if neptunium removal and adsorption were due to ion exchange.

TABLE 3-48. PROPERTIES OF SOIL SAMPLES (ROUTSON ET AL., 1976)

Soil	$CaCO_3$, mg/g	Silt, wt%	Clay, wt%	CEC, meq/100 g	pH
Washington Soil (Burbank sandy loam)	0.8	10.1	0.5	4.9	7.0
South Carolina Subsoil	<0.2	3.6	37.2	2.5	5.1

TABLE 3-49. NEPTUNIUM Kd (ml/g) AS A FUNCTION OF SOIL AND SOLUTION (ROUTSON ET AL., 1976)

	Ca		Na	
Soil	0.002 M	0.2 M	0.015 M	3.00 M
Washington	2.37	0.36	3.9	3.2
South Carolina	0.25	0.16	0.7	0.4

Sheppard et al. (1976) determined neptunium distributions on several Washington and North Carolina soils. The distilled water-trace ^{237}Np solutions and soils were equilibrated over long periods of time to obtain a rate of change per month in the distribution values. The 50-day values are given in Table 3-50. A positive value for the monthly change in the distribution means an increase in the size of the distribution value. The distribution was determined in the same way that a Kd value is determined, but does not have the connotation that equilibrium has been attained as the Kd does.

TABLE 3-50. NEPTUNIUM 50-DAY DISTRIBUTION VALUES COMPUTED FROM SHEPPARD ET AL. (1976)

Soil Identity	Np Distribution, ml/g	Monthly Change in Distribution
Muscatine silt loam	127	+10%
Burbank loamy sand	15.4	+48%
Ritzville silt loam	20.2	+28%
Fuquay sand 0-5 cm depth	33.7	+25%
Fuquay sand 5-15 cm depth	37.2	+25%
Fuquay sand 15-50 cm depth	32.4	+19%

The neptunium Kd value of about 3.9 ml/g was given by Routson et al. (1975, 1976) for the Burbank sandy loam without sodium in the solution. Sheppard et al. (1976), apparently for the same conditions, gives a neptunium 50 day distribution value of 15.4 ml/g for Burbank and states that this value is increasing at the rate of +48%/month. At 100 days, the distribution was approximately 50 ml/g on the Burbank loamy sand. The differences in neptunium distribution between soil and solution probably resulted from the experimental differences because the Burbank sandy loam of Sheppard was obtained from Routson. However, Sheppard shows the Burbank of his sample to contain 21.2% silt and 2.8% clay with a pH of 8.1 and a cation exchange capacity of 5.94 meq/100 g compared to Routson's Burbank soil sample (Table 3-48). Sheppard's Burbank must have contained calcite ($CaCO_3$) to attain a pH of 8.1.

There is no evidence in Sheppard et al. (1976) that the soil samples were pre-equilibrated in any way with the nonradioactive solution before the neptunium tracer was added, or that a blank solution without the soil was run with the soil equilibrations for reference and use in counting as the original solution condition without the soil present. In addition, Sheppard reported that his ^{237}Np(V) in the aqueous phase equilibrating with Ritzville soil was partially filterable on Whatman number 50 filter paper. Routson, on the other hand, reported that upon filtering previously centrifuged samples of solution containing neptunium and in contact with Burbank or South Carolina subsoil through 0.01 and 0.45 μm filters, no evidence of colloidal ^{237}Np was found. This is further evidence that Sheppard's high neptunium distribution values require further elucidation in the light of Routson's results.

Migration Results

Field Studies--

No reports of field studies of neptunium migration through soil or rock were found in the literature.

Laboratory Studies--

No reports of laboratory studies of neptunium migration through soil or rock were found in the literature.

Summary

The existing thermodynamic data (Figure 3-14) show that neptunium should exist in an oxidizing soil environment as Np(V) in the form of NpO_2^+. However, existing adsorption results, essentially only a study by Routson et al. (1975, 1976) and Sheppard et al. (1976), inferred that there is little evidence of NpO_2^+ ion exchange as a neptunium adsorption mechanism. Sheppard et al. (1976) reported neptunium colloids present in the soil-solution environment, while Routson et al. (1975, 1976) specifically showed that they were absent from his solutions that had contacted soils. It is fairly certain that neptunium Kd values are generally low. Little more can be said based on the adsorption and migration studies now available in the literature. Additional research is required on neptunium-soil and rock reactions.

References

Bensen, D. W. 1961. Mineral Adsorption of Radionuclides in Reactor Effluent. HW-69225.

Burney, G. A. and R. M. Harbour. 1974. Radiochemistry of Neptunium. NAS-NRC Nuclear Sci. Ser. NAS-NS-3060.

Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie GmbH.

Robertson, D. E. 1974. Physicochemical Characterization of N-Reactor Effluent Radionuclides in Soil and Water Systems. BNWL-1950, Pt. 2, pp. 82-85.

Routson, R. C., G. Jansen, and A. V. Robinson. 1975. Sorption of ^{99}Tc, ^{237}Np, and ^{241}Am on Two Subsoils from Differing Weathering Intensity Areas. BNWL-1889.

Routson, R. C., G. Jansen, and A. V. Robinson. 1976. ^{99}Tc, ^{237}Np, and ^{241}Am Sorption on Two Subsoils from Differing Weathering Intensity Areas. BNWL-2000. Pt. 2, pp. 50-52.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Sheppard, J. C., J. A. Kittrick, T. L. Hart. 1976. Determination of Distribution Ratios and Diffusion Coefficients of Neptunium, Americium and Curium in Soil-Aquatic Environments. RLO-221-T-12-2.

PLUTONIUM

Natural Soil and Rock Distributions

Except for very small quantities of plutonium in the natural environments given below, plutonium does not occur in any significant amount in soils or rocks. Cherdyntsev et al. (1968), for example, lists ^{239}Pu values in natural rocks and minerals varying from 7 x 10^{-12} g ^{239}Pu/g to 1 x 10^{-15} g ^{239}Pu/g.

Brief Chemistry

Fifteen isotopes of plutonium are known, including 10 isomers with different decay modes (Keller, 1971). Most of the isotopes are formed by multiple neutron capture, and therefore, are not ordinarily encountered in natural environments. An exception is the natural reactor at Oklo, Gabon (IAEA, 1975) and very small amounts (Pu/U = 10^{-11}) found in the uranium mineral pitchblende (Cleveland, 1970).

The plutonium isotopes of concern to waste disposal, either because they are contained in the fission product wastes or are a part of an impotant decay chain for waste constituents, are listed in Table 3-51. In the short term, almost any plutonium radionuclide would be of concern in waste-radionuclide reactions although, on a weight basis, longer-lived ^{242}Pu is not nearly as hazardous as ^{239}Pu. Long irradiation times and high neutron fluxes are required to produce significant amounts of ^{242}Pu, so that a prevalence of the higher mass Pu isotopes usually will not occur in waste solutions from commercial fuel treatment facilities.

TABLE 3-51. PLUTONIUM RADIONUCLIDE DATA (KELLER, 1971)

Isotope	Half-Life	Decay Mode
^{236}Pu	2.85 years	α, SF
^{238}Pu	86.4 years	α, SF
^{239}Pu	24,400 years	α, SF
^{240}Pu	6,600 years	α, SF
^{241}Pu	14.1 years	β^-, α
^{242}Pu	387,000 years	α
^{243}Pu	4.98 hours	β^-

Plutonium exists in five oxidation states in aqueous solutions that include Pu(III), Pu(IV), Pu(V), Pu(VI) and Pu(VII). These states can occur as the hydrated ions Pu^{+3} · aq, Pu^{+4} · aq, PuO_2^{+} · aq, PuO_2^{+2} · aq and PuO_5^{-3} · aq (Keller, 1971). The most stable state of plutonium in aqueous solution is Pu(IV). However, disproportionation, in which Pu(III), Pu(IV), Pu(V) and Pu(VI) states can coexist in unequal quantities, tends to further complicate plutonium chemistry in its reactions with soils and sediments. According to Cleveland (1970), plutonium in near-neutral solutions occurs in the order: $Pu^{+4} > PuO_2^{+2} > Pu^{+3} > PuO_2^{+}$. Hydrolysis reactions lead to the formation of positively charged to neutral colloidal polymers in a stepwise manner. For example, $Pu^{+4} + OH^- \rightarrow PuOH^{+3} + OH^- \rightarrow Pu(OH)_2^{+2}$, etc., leads finally to $Pu(OH)_4$ which loses water to product thermodynamically stable PuO_2 (Keller, 1971). The kinetics of the hydrolysis reactions leading to PuO_2 are not known. It is known that depolymerization of colloidal Pu(IV) is a very slow process, having a "depolymerization half-life" of 320 hr at 25°C in 5M HNO_3 (Keller, 1971). Complexing agents such as fluoride or sulfate ions can accelerate the process. Plutonium can form complexes with most of the ions commonly encountered in soil solutions. Thus disproportionation, complex formation and hydrolysis reactions, all relatively pronounced with aqueous plutonium solutions, combine to add to plutonium chemistry complexity.

Solid Phase and Solution Equilibria

Figure 3-15 relates the activity of Pu^{4+} to pH in an oxidizing environment [$pO_{2(g)}$ = 0.68 atm] in equilibrium with various Pu solid phases. The parameters indicated in parentheses after the mineral formulas refer to the additional conditions of equilibrium. For example, (V&G) indicated after the $Pu(HPO_4)_2$ mineral formula denotes that the mineral is considered to be in equilibrium with variscite and gibbsite. Any solid in Figure 3-15 that lies below another solid, at a given pH, is the more stable. Thus, for any two solid phases at a specific pH, the solid that maintains lower Pu^{4+} activity is more stable. Under the assumptions outlined in Figure 3-16 and at pH 6, the plutonium compounds in order of increasing stability are: $Pu(OH)_3$; βPu_2O_3; PuF_4; PuF_3; $Pu(HPO_4)_2$; PuO_2OH; PuO_2CO_3; $Pu(OH)_4$; $PuO_2(OH)_2$; and PuO_2. Amont the solids reported in Figure 3-15, PuO_2 is the most stable mineral under oxidizing conditions at all pH values.

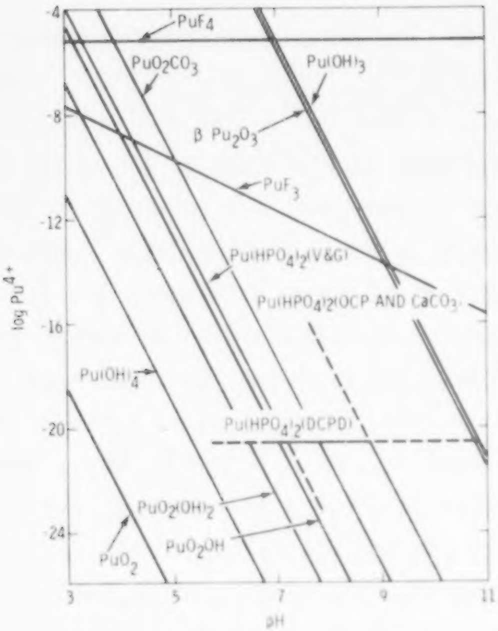

Figure 3-15. The relative stability of various plutonium solids in an oxidizing environment [$pO_2(g)$ = 0.68 atm], $pCO_2(g)$ = 3.52 atm, pF^- = 3.5 and phosphate levels in equilibrium with Variscite and Gibbsite (V&G) Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP) (Rai and Serne, 1977)

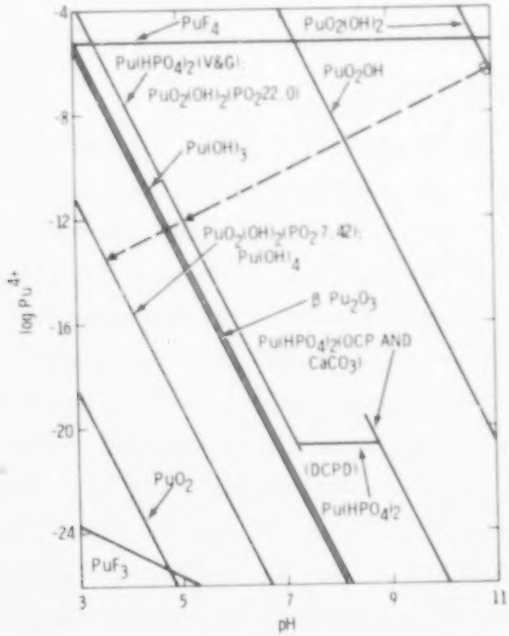

Figure 3-16. The relative stability of various plutonium solids in a very reducing environment [$pO_2(g)$ = 80 atm], $pCO_2(g)$ = 3.52 atm, pF^- = 3.5 and phosphate levels in equilibrium with Variscite and Gibbsite (V&G) Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP) (Rai and Serne, 1977)

The stabilities of plutonium solid compounds in a reducing environment [$pO_{2(g)}$ = 80 atm] are represented in Figure 3-16. In general, the reducing environment substantially changes the stabilities of the solids. Comparing Figures 3-15 and 3-16, it can be seen that the Pu(IV) solids remain unchanged, while Pu(III) solids increase and Pu(V and VI) solids decrease in their stabilities with the decrease in the oxygen pressure. Plutonium solids in the reducing environment at pH 6 can be arranged in order of increasing stability as follows: $PuO_2(OH)_2$; PuO_2OH; PuF_4; $Pu(HPO_4)_2$; $Pu(OH)_3$; βPu_2O_3; $PuO_2(OH)_2$; PuF_3; and PuO_2. PuF_3 would be the most stable solid compound below pH 4. Above this pH value, PuO_2 would be the most stable solid (Figure 3-16). Based upon the Eh-pH diagrams for plutonium oxides, and hydroxides, Polzer (1971) predicted $PuO_2(s)$ to be the most stable solid phase under conditions generally found in the environment. However, the relative stabilities of Pu compounds other than hydroxides and oxides, and predictions regarding weathering sequences, were not considered by Polzer (1971).

Knowledge of the most stable compound present in the soil is necessary in order to predict the behavior of fate of the element in the soil. An extensive review on actinides indicated that numerous workers have studied the plutonium concentration and distribution with depth in soils. However, with the exception of Price and Ames (1975), none have made any attempt to identify the solid phases of plutonium present in soils. Price and Ames (1975) reported the presence of PuO_2 under both alkaline and acidic oxidizing environments. Their observations were made approximately 20 years after the acidic radioactive waste was disposed to the alkaline soils. Tamura (1974) inferred the presence of PuO_2 in aridisols or entisols from the Nevada Test Site. Thus, the Price and Ames, and Tamura results confirm theoretical predictions made regarding the most stable plutonium compound expected to be present in soils. However, if the soil solution activity of plutonium is lower than the solubility product of PuO_2 and any other possible compound, the final solution activities will depend mainly on cation exchange processes and the coprecipitation of plutonium with other soil minerals.

Figure 3-18 demonstrates the activity of various plutonium species expected in equilibrium with $PuO_2(s)$ and in an oxidizing environment (pO_2 16 atm). Plutonium in solution exists in four oxidation states (Pu^{3+}, Pu^{4+} PuO_2^+,

PuO_2^{2+}) and forms complexes with OH^-, Cl^-, F^-, SO_4^{2-}, $H_2PO_4^-$ and Co_3^{2-} ions. In general, the activity of all positively charged ions and ion-complexes and a few neutral ion-pairs decreases with the increase in pH, while the activity of all negatively charged ion-complexes increases with the increase in pH. In an oxidizing environment, Pu^{3+} and Pu^{4+} and their ion-pairs have an insignificant effect on the total activity of plutonium in solution. At any given pH, the total activity of plutonium in solution can be obtained by adding the appropriate activities of various plutonium species. Since the lines for some plutonium species are based on concentration constants, the position of the lines may change when converted to thermodynamic equilibrium constants. Figures 3-17 and 3-18 were constructed by assuming a weathering environment (pCO_2 = 3.53; pCl^- = pSO_4^{2-} = 2.5; pF^- = 3.5) and $PuO_2(s)$ as the compound that may be present in the soil at equilibrium. When diagrams are constructed for an actual weathering environment of a given soil, all the organic and inorganic ligands present in the soil solution should be considered. Figures 3-17 and 3-18 were developed for selected inorganic ligands only.

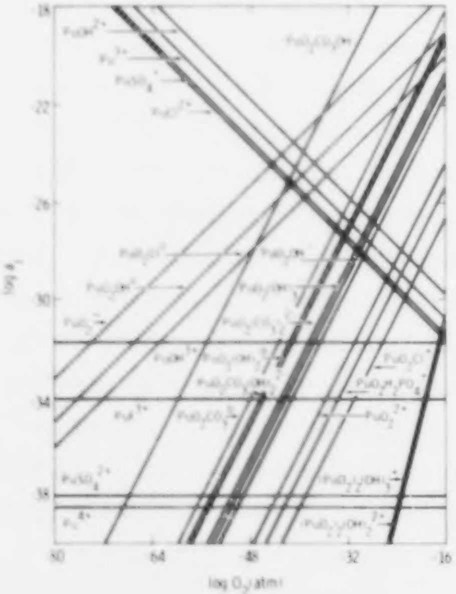

Figure 3-17. The activity of various plutonium species in soil solution in equilibrium with $PuO_2(s)$ at pH 8, pCO_2 = 3.52 atm, pCl^- = $pSO_4{}^{2-}$ = 2.5 and $pH_2PO_4{}^-$ = 5.0 (Rai and Serne, 1977)

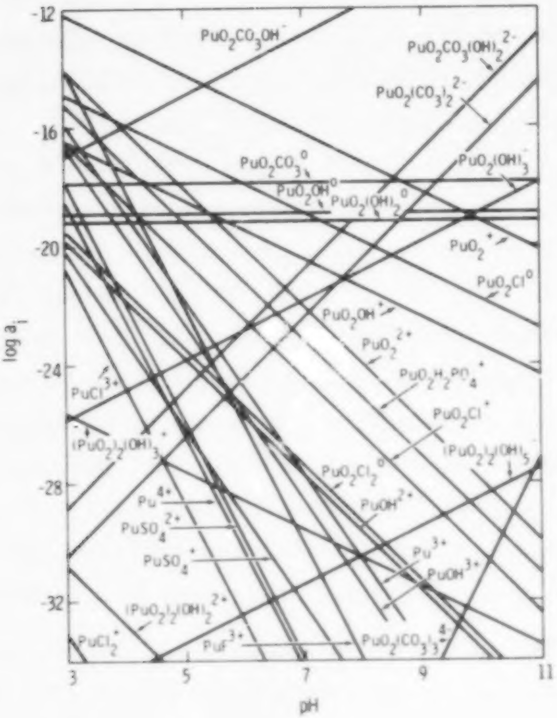

Figure 3-18. The activity of various plutonium species in soil solution in with $PuO_2(s)$ in a mildly oxidizing soil environment [pO_2 = 16 atm], pCO_2 = 3.52 atm, pCl = 2.5, pF^- = 3.5 and pH_2PO_4 = 5.0 (Rai and Serne, 1977)

Figure 3-17 relates the activities of (a_i, moles/liter) of various solution species at pH 8 to the oxidation potential as represented by the various oxygen pressures. In general, with a decrease in oxygen pressure (increase in reducing conditions), the kind of activity of the solution species changes: 1) Pu^{3+} species increase in activity, 2) Pu^{4+} species are unaffected and 3) PuO_2^+ and PuO_2^{2+} species decrease in activity. However, in doing so, the total activity of plutonium in solution at any given pH would not change significantly because the activity of species for which thermodynamic equilibrium constants are known is very large as compared to the others. When the concentration constants are converted to thermodynamic constants, the new lines would shift downward or upward but remain parallel to the present lines. The activities of various species would still vary in the same direction with the changes in pH as reported in Figure 3-18.

A few of the reactions are not plotted in the figures because either the activities of the species fall beyond the graph boundaries or the equilibrium constant data are not reliable. Cleveland (1970) suggested that the values for the formation constants of $PuCO_3^{2+}$ and $Pu(OH)_4^\circ$ were suspect; the values for $PuO_2(OH)_3$, $PuO_2^0(O)_2^\circ$, and PuO_2OH^+ should be viewed with skepticism; and the value for PuO_2OH° should be considered only approximate. Under the assumptions of Figure 3-18, the lines for $Pu(OH)_4^\circ$ and $PuO_2(OH)_2^\circ$ would be parallel to the X-axis with $10^{-12.51}$ and $10^{-19.16}$ moles/l activity, respectively. Many researchers (Andelman and Rozzell, 1970; Fukai and Murray, 1974; Grebenshchikova and Davydov, 1961, 1965; Sheidina and Kovarskaya, 1970) have reported that plutonium in solution also exists as colloidal species over a wide pH range. Colloidal species and neutral ion-complexes [$Pu(OH)^\circ{}_4$, $PuO_2(OH)^\circ{}_2$] are not reported in Figures 3-17 and 3-18. If present in large quantities, these species would significantly influence the nature of the species and the total concentration of plutonium in solutions.

For the conditions specified in Figure 3-18, the dominant plutonium species in low and high pH ranges are PuO_2^+ and $PuO_2CO_3OH^-$, respectively. The colloid complex of soils is mainly negatively charged. Therefore, positively charged species are usually absorbed by soils in cation exchange processes. Since positively charged PuO_2^+ species predominate only in solutions of pH values <6, cation exchange adsorption of plutonium by soils would be limited to acidic soils (pH <6). The negatively charged $PuO_2CO_3OH^-$ complex that predominates above pH 8 [even when the activity of $PuO_2CO_3OH^-$ is compared to $Pu(OH)^\circ{}_4$] should not be readily adsorbed by the soils. Thus, the activity of plutonium in soil solutions of pH >8 would be relatively high because of: 1) little soil adsorption of negatively charged ions and 2) increases in the activities of negatively charged ions with the increase in pH. Similarly, under extremely low pH conditions the activity of plutonium in soil solutions in equilibrium with $PuO_2(s)$ may also be high. Rhodes (1957) found low adsorption of plutonium by soils in the pH range of approximately <2 and 8-13. Thus, his results confirm part of the predictions based on Figure 3-18; continuous decrease in adsorption is predicted with the increase in pH above 8, whereas Rhodes' data indicated first a decrease in adsorption to pH 12 and then an unexplained continuous increase in adsorption above pH 12.

It should be mentioned that in addition to cation exchange, the total retention of plutonium wastes percolating through soils would depend on many other factors, such as flow rate, precipitation of solid phases, physical entrapment of particulate and colloidal plutonium, soil properties, and wastewater composition. Therefore, the above adsorption predictions based only on cation exchange should be viewed as an approximation. As the data on actual adsorption isotherms and mechanisms and various soil-actinide interactions accumulate, more accurate predictions will be possible.

Experimental Adsorption Results

Thorburn (1950) reported a sorption experiment in which plutonium in water was percolated through a soil column. The soil was then wet sieved and the activity of each particle size fraction counted. In general the decrease in particle size increased the amount of Pu adsorbed (Table 3-52). In other adsorption experiments, Thorburn placed small aliquots of actual plutonium waste on top of soil columns and eluted with distilled water or saturated magnesium-calcium carbonate. There were no significant differences in the elution curves. It is interesting to note that the elution curves had higher plutonium activity in the first volume out of the column and always showed a small leakage which might signify physical transport of fine particulates, neutral polymers or colloids. Thorburn took the effluent from the distilled water leached column and percolated it through a second soil column at various flow rates. The data show that Pu concentration in effluents through the second column varied with flow rate. The faster the flow the more plutonium in the effluent. Filtration of the influent through a fine filter paper did not change the results. Explanations of these phenomena are obscure but would seem to indicate plutonium transport as polymer. Final adsorption studies of plutonium in water versus pH by soil columns showed 87% adsorption at pH 3.8, 77% at pH 7.2 and 24% at pH 10. Note that this falling of plutonium adsorption with increasing pH is supported by the thermodynamic data of Figure 3-18.

Evans (1956) reported percentage of plutonium removed from a 0.001 N HNO_3 solution by various grain sizes of quartz. The plutonium Kα values may be computed from these data, and are listed in Table 3-53. Data also were given on plutonium adsorption on different minerals of coarse clay size (2 to 0.2 μm).

TABLE 3-52. PLUTONIUM ADSORPTION VERSUS PARTICLE SIZE (THORBURN, 1950)

Size, mm	Pu, d/min/g
>1.19	39.3
1.19 - 0.25	--
0.25 - 0.15	1,171
0.15 - 0.10	929
<0.105	8,578
Uncentrifugible Silt and Clay	62,750

TABLE 3-53. PLUTONIUM Kd VALUES FOR QUARTZ OF VARIOUS PARTICLE SIZES FROM A 0.001 N HNO_3-PLUTONIUM SOLUTION (EVANS, 1956)

Quartz Particle Sizes	Kd, ml/g
Coarse sand	5.6
Fine sand	10.0
Coarse silt (50-20 μm)	11.3
Medium silt (20-5 μm)	33.5
Fine silt (5-2 μm)	48.8
Coarse clay (2-0.2 μm)	80.9

Plutonium Kd values were computed from these data and are listed in Table 3-54. Evans suggested that the lower Kd for plutonium by montmorillonite is probably due to experimental difficulties and believed that Rhodes' (1955) data may represent preferred plutonium Kd results. Rhodes' data, as reported by Evans, are given in Table 3-55, assuming a 1 ml to 1 g solution to soil ratio. This ratio was not given, but the results are proportional in any case.

Rhodes (1952, 1957a, 1957b) performed similar plutonium Kd determinations on a Hanford sand soil (92% sand) with 2% calcium carbonate content. Using a soil to solution ratio of 1:20 and neutral pH, Rhodes found rapid adsorption. Analysis versus time yielded an equation for the amount adsorbed versus contact

TABLE 3-54. PLUTONIUM Kd VALUES FOR DIFFERENT MINERALS OF COARSE CLAY SIZE (2 to 0.2 μm) FROM 0.001 N HNO_3-PLUTONIUM SOLUTION (EVANS, 1956)

Mineral	Kd, ml/g
Feldspar	170.4
Quartz	82.0
Glauconite	∞
Montmorillonite	157.0
Kaolinite	1091.0

TABLE 3-55. RHODES' PLUTONIUM Kd DATA AS REPORTED BY EVANS (1956)

Material	Kd, ml/g
Montmorillonite	4990
Fine micaceous sand	49
Kaolinite	42.5
Soil	36
Coarse sand	0.87

time, $\%Pu_{ADS} = 81 + 5.2 \log time_{(min)}$. For example, after 1 min, 20 min and 60 min, 81%, 88%, and 90%, respectively, of the solution plutonium concentration was adsorbed. Increases in the soil to solution ratio were also observed to increase the percent adsorbed. Rhodes also obtained adsorption versus pH data and found rapid decreases in adsorption below pH 2 but almost total adsorption (Kd > 2000) between pH 3 and 8.5. Decreases at pH 10 to 12 were believed to indicate changes in plutonium speciation. In other experiments, coarse sand was observed to adsorb only 47% of the plutonium present compared to 97 to 99.8% for soils and clay minerals. Rhodes felt all these data indicated ion exchange adsorption mechanisms. Yet plutonium adsorption from distilled water, a synthetic high salt waste and an actual high salt waste all showed greater than 98% removal. Plutonium solution loading experiments onto soil columns at various pH's (1, 4, 10) showed good removal at the first two pH's until the high acid case had destroyed the $CaCO_3$ buffering capacity. As the effluent pH dropped to pH 1, increasing plutonium breakthrough was observed. Plutonium breakthrough at pH 10 was highly variable and rapid, possibly caused by fine plutonium particulate dispersion or polymer formation. Plutonium adsorption from distilled water, 4M $NaNO_3$ and $2M(NH_4)_2HPO_4$ solutions was above 96%, but a 4M ammonium acetate solution showed only 59% adsorption. Acetate complexing of plutonium was probably responsible for the diminished adsorption rather than any effects from competing ions.

Further studies showed increasing the acetate concentration from 0.01M to 8M dropped plutonium adsorption from 74% to 21%. Acetate solutions were also observed to have the capability of extracting plutonium adsorbed on soils. Bensen (1960) presented data showing that oxalate salts also inhibit plutonium adsorption by soluble Pu-oxalate complex formation. Bensen also re-interpreted Rhodes' data and concluded precipitation reactions, not ion exchange, probably control plutonium adsorption on soils.

Other investigations on plutonium were performed at Savannah River by Prout (1958, 1959). Plutonium adsorption by a soil (80% sand-20% clay) with the clay mineral kaolinite dominant was determined versus pH for distilled water traced with plutonium ($\sim 10^{-6}$M). The soil/solution ratio was 1:10 and the mixtures shaken for 2 hr before phase separation by centrifugation. Adsorption of plutonium depended on pH and the valence state of the plutonium added to solution. Adsorption was more than 90% complete from solutions of Pu(III) and Pu(IV) between pH 2.5 and 12 and from solutions of Pu(VI) at pH's greater than 6. Strong adsorption at mildly acidic to mildly basic pH's is probably due to a combination of cation exchange and precipitation of hydrolysis products. Decreased adsorption above pH 9 possibly represents the formation of soluble negatively charged Pu polymers which do not readily exchange with the soil.

Knoll (1965, 1969) and Hajek and Knoll (1966) reported studies on high salt wastes with organic contaminants typical of fuel reprocessing. An acid (0.3M) high salt (5.4M NO_3^-) waste spiked with actual americium and plutonium wastes were percolated through soil columns. After 0.3, 1.5 to 4.0, and 20 column volumes of effluent, the plutonium breakthrough was 20 to 30%, 50%, and 70 to 98%, respectively, for several columns. Batch adsorption tests on the high salt acid wastes from storage tanks showed low adsorption Kd values of from 2.4 to 2.9 ml/g with resultant soil pH's of 2 to 3. If the waste was neutralized and the supernatant was used in batch adsorption tests, the Kd increased. Addition of suspected organic contaminants to a concentration of 20% by volume decreased the Kd for the neutralized waste to 1.4. Water leachates of the sludge produced on neutralization contained some plutonium. Upon soil contact the Kd for this leachate rose to 1540 ml/g. If the high salt acid waste was neutralized in the presence of molar quantities of citric acid, no precipitation was observed. If this citrate-neutralized waste was percolated through soil columns, most of the plutonium was removed. A constant low leakage percentage of plutonium was observed and may have been caused by a solubility or particle transport mechanism.

In other experiments (Knoll, 1969) tap water spiked with plutonium was percolated through soil columns to allow plutonium adsorption. The soil columns were then leached with various organics: TBP-CCl_4, DBBP-CCl_4, Fab Oil, D2EHPA in hydrocarbons C_{10}-C_{14}, and hydroxyacetic acid. These organics are all commonly used in various process streams during fuel reprocessing. TBP in carbon tetrachloride after 130 column volumes had caused only 5% of the soil sorbed plutonium to leach; DBBP removed 40% of the soil sorbed plutonium in 80 column volumes; Fab Oil removed less than 4% in 30 column volumes; D2EHPA removed about 30% of the plutonium; and hydroxyacetic acid removed no less than 40% of the plutonium depending on the acid concentration. When the plutonium was added to the organics and then percolated through the soils, very little soil adsorption was observed.

Many investigations have been performed on plutonium adsorption by sediments in both fresh and marine waters. Schneider and Block (1968) found plutonium to adsorb more than I^- and Sr^{+2} but less than Zn^{+2} or Cs^+ on Rhine River sediments. Equilibrium was reached within 24 hr.

The location of plutonium at ground disposal sites on the Hanford Reservation has been closely monitored for over 20 years. Liquid wastes disposed to the unsaturated sandy soil in several instances included trace amounts of plutonium. Typically, plutonium has not been found to percolate through the soils to any extent. Typical data (Brown, 1967) show 99.9+% of long-lived radionuclides such as plutonium to be adsorbed within the first 10 m of soil.

Crawley (1969) reports on plutonium penetration at two facilities. Plutonium in a sand to which slightly acidic high salt wastes were released had penetrated at least 18 ft. Plutonium in a sand to which neutralized low salt water had been released penetrated less than 2 ft.

Desai and Ganguly (1970) determined the ability of humic and fulvic acid in ammoniacal solutions to solubilize plutonium. In this basic solution without humic or fulvic extract, only 13% of added plutonium remained in solution; with humic extract 54% of the added plutonium remained in solution; and further testing showed that the soluble plutonium was noncationic. The fulvic acid extract solubilized 58% of the plutonium, and again the complex was noncationic.

Rozzell and Andelman (1971) studied the adsorption-desorption of aqueous plutonium (10^{-8} to 10^{-7}M) on quartz and other silica surfaces. Adsorption continued typically for 12 to 15 days before apparent equilibrium was reached. At pH 7, adsorption increased with increasing ionic strength, but decreased when HCO_3^- was added. The amount of adsorption varied at pH 5 and 7, but differently at high and low ionic strengths, as well as with age of the solution. Plutonium desorption indicated that there were two basically different adsorbed species. There was a great net desorption at pH 5 versus pH 7 to 9.

Tamura (1972) discussed the adsorption of plutonium on several materials including the soil constituents listed in Table 3-56. The suspension pH represents the final system pH.

TABLE 3-56. REMOVAL OF PLUTONIUM FROM pH 7 WATER BY SEVERAL SOIL MINERALS (TAMURA, 1972)

Constituents	Kd, ml/g	Suspension pH
Attapulgite	4,370	9.60
Montmorillonite	630	9.20
Alumina, activated	755	8.35
Kaolinite	352	6.25
Illite	129	5.90
Quartz	0	6.35

Fried et al. (1973, 1974, 1974) found that plutonium adsorbed on limestones, shales, and sandstones would very slowly migrate through the pores. The velocity of migration relative to the leaching water was 3×10^{-5} for limestone and 6×10^{-5} for basalt. If the leaching solution was saturated with CO_2 an increased elution from the limestone and sandstone was observed. Studies of plutonium movement along a fissure crack in basalt shows plutonium movement in two phases: the slower moving phase adsorbs similar to Pu^{+4}, but a faster moving phase with only about 1/10 the tendency to adsorb was also observed. Fried et al. hypothesized a polymeric state for this phase.

Fried et al. (1974, 1974) immersed disks of limestone and basalt in $Pu(NO_3)_4$ solution at 4×10^{-5}M Pu. After equilibration the activity in the solutions was re-measured. Losses in plutonium were equated to adsorption on the rocks. Basalts adsorbed more plutonium than limestone on a surface area basis. The effects of salt solutions of Na^+, Ca^{++}, Sr^{++}, La^{+3}, and Zr^{+4} were also studied. In all cases the salts displaced some of the plutonium from the rocks. The higher the concentration and the larger the valence charge, the easier was the displacement. This was similar to the trends expected for ion exchange mechanisms. A leaching study showed eight column volumes of 0.5M HCl removed 30% of the plutonium adsorbed on shale. Eight additional column volumes of 4M HCl removed an additional 20%.

Two review articles which contain discussions on adsorption reactions of plutonium and soils are available, Francis (1973) and K. Price (1971, 1973).

Ames (1974), Price and Ames (1975) and Ames (1976) characterized the actinide-bearing sediment underneath a liquid waste disposal facility which received high salt, acidic wastes. The distribution in plastic impregnated core samples showed a surface soil plutonium concentration of near 0.5 mCi $^{239}Pu/g$. This concentration decreases to about 0.6 μCi $^{239}Pu/g$ within the first 2 m of underlying sediment and to less than 60 pCi/g at the maximum depth sampled (9 m). Examination of the contaminated soils showed at least two types of plutonium present: 1) discrete PuO_2 particles (>70 wt% PuO_2) and 2) plutonium (<0.5 wt% PuO_2) associated with silicate hydrolysis. The PuO_2 particulate form "filtered out" within the upper 1 m of sediment. The "hydrolysis" type of plutonium penetrated deeper within the sediment and deposited in association with silicate hydrolysis products as the soil minerals reacted with the acid waste. The highest concentrations of nonparticulate plutonium about 1 m below the bottom of the disposal facility receiving acidic wastes were associated with smectites present in the soil before waste solution disposal. The smectites higher up in the column tended to be partially to totally altered because of the acidic nature of the waste solutions. Plutonium was uniformly distributed in the sectioned smectite particles, suggesting adsorption of charged plutonium species by the clays.

Emery and co-workers (1974, 1974, 1975) have studied the ecological behavior of one Hanford liquid waste pond. Ninety-five percent of the incoming low-level waste percolates through the desert sands. The sediments are the principal repository, with the top 10 cm containing an average 390 pCi Pu/g. The overlying water contains 0.01 pCi Pu/l. Assuming that these values constitute equilibrium conditions, an estimate of the plutonium Kd can be made. The resultant Kd value is 3.7×10^7 ml/g. Plutonium in the interstitial waters appears to be mainly cationic or nonionic forms. Plutonium in the pond water appears to be mainly fine particulates possibly signifying that the waste stream plutonium content is predominantly PuO_2 particles.

Miner et al. (1973, 1974), Polzer and Miner (1974, 1977) and Glover et al. (1977) described experiments in progress to measure the adsorption of both "soluble" plutonium and particulate plutonium (PuO_2) in numerous soils at three plutonium levels between 10^{-6} and 10^{-8}M. The plutonium adsorption was rapid and quite high: 59% of the time, adsorption was greater than 99% (Kd > 430) and only 5% of the time was it below 90% adsorption (Kd < 39). Correlations were found between soil characteristics associated with soil ion exchange or acidity. The adsorption also depends on the initial plutonium concentrations for which several possible causes are discussed including precipitation with increasing plutonium concentration and the formation of carbonate complexes.

Experiments at Savannah River (Savannah River Laboratory, 1975) with degraded TBP-DBBP-kerosene wastes containing plutonium showed rapid migration through soils (Kd ∿ 0.4 ml/g). When small portions of the solvent waste were allowed to dry on soils and leached by groundwater, however, very little plutonium migration was observed (Kd ∿ 6000 ml/g) in the effluent.

Duursma et al. (1971, 1973, and 1974) have determined the adsorption of plutonium in the marine environment. The adsorption of plutonium is intermediate; less than Cs, Rb, Zn, Fe, Zr-Nb, Ru and Pm and greater than Ca and Sr. Plutonium has been observed to penetrate sediments at least to 8 to 14 cm, and in the early 1970's, inventories in the sediment appear to show losses. Biological processes or upward migration in interstitial waters as a reduced species are two possible explanations, although Mo and Lowman (1975) showed data which find reducing conditions tend to lower plutonium mobility. Changes in the americium to plutonium ratio from waters to sediments in the ocean led Duursma to conclude americium is preferentially adsorbing or not being remobilized as fast as plutonium. In seawater $PuO_2(CO_3)_3^{-4}$ may predominate and cause the lower plutonium adsorption. Using a ^{237}Pu tracer in valence states +3, +4, and +6 in both oxic and anoxic seawaters at pH 7.8 to 8.0, Duursma found the Kd for marine sediments to be about 10^4 ml/g. Valence states and solution Eh did not cause marked differences.

Fukai and Murray (1974) performed plutonium adsorption-desorption experiments for both freshwater and saline conditions. Plutonium (III) adsorption experiments from river water to river sediments (100 ml traced solution/g sediments) were performed. The initial stage of adsorption was rapid; 50% within 10 hr. For pH 3 to 11 over 90% of the Pu(III) was adsorbed by the river sediment. Desorption experiments were performed wherein the sediments used in the adsorption experiments were suspended in seawater. Over the pH range 4 to 10 about 10% of the adsorbed plutonium was released without apparent pH differences. Similar adsorption-desorption experiments were performed with river sediments contacted with various dilutions of freshwater sewage effluent at pH 8.1. The Pu(III) adsorption increased from 85% in river water to over 95% at 100% sewage effluent. These sediments were next contacted with seawater and desorption monitored. At equilibrium, river sediments that had not been contacted with sewage effluent released only 5% of the plutonium, whereas sediments contacted with 5 to 100% by volume sewage effluent released 12%.

Van Dalen et al. (1975) determined the plutonium distribution coefficient, Kd, for several Dutch subsoils from 90% saturated NaCl solutions between pH 7 and 8. Clay samples of mainly illite and kaolinite had a Kd of $\sim 10^4$ ml/g and for a river sand a Kd of 200 ml/g. Gypsum-bearing and clay-bearing sandstones were intermediate. The pH dependence on adsorption of plutonium was minor between pH 5 and 8.

Mo and Lowman (1975) placed plutonium-contaminated calcareous sediment in aerated seawater and anoxic seawater and stirred the system until solution activities were at equilibrium. The resultant plutonium Kd values were 1.64 x 10^4 and 3.85 x 10^5 ml/g.

Tamura (1975, 1975) evaluated the plutonium content of various size fractions of contaminated Nevada Test Site and Oak Ridge soils and Mound Laboratory sediments. These results should be considered exploratory in nature because the results are based on only a few observations; the source terms differed; and the particle size fraction separations were technique dependent. The NTS soils showed different particle sizes with plutonium associations depending on location from ground zero. In general, the coarse silt (20 to 53 μm) and medium silt (5 to 20 μm) fractions contained about 80 to 85% of the total plutonium. The Oak Ridge plutonium was more evenly distributed in the silt and clay sizes, with clay slightly higher. The Mound Laboratory sample showed 70% of the plutonium in the clay fraction.

Bondietti et al., (1975) found purified soil humates to absorb plutonium strongly, 99.9+% while reference clays (montmorillonite and kaolinite) adsorbed about 98 and 96% of plutonium added to a water solution at 163 μg Pu/g of solid. If the organic matter and iron oxide coating were removed from clay material, plutonium adsorption was 95% versus 99.9% while intact. Leaching solutions, citrate, DTPA, and fulvate removed small amounts of adsorbed plutonium as shown in Table 3-57. Thus, it appears that natural soil organic matter can very strongly adsorb plutonium. The ability of soil organic matter to alter the oxidation state of plutonium in soil water solutions was also verified. Pu(VI), and by inference Pu(V), were unstable in the presence of fulvic acid, polygalacturonic acid and alginic acid. Positive proof of reduction to Pu(IV) was shown at environmental pH's 6.5 to 8. Plutonium (IV) was the most stable valence upon interaction with these organics. Further reduction of Pu(IV) to Pu(III) occurred in the presence of humic or fulvic acids, but was not observed above pH 3.1 under aerobic conditions. Bondietti also demonstrated that plutonium is at least partially associated with humic materials in ORNL soil contaminated 30 years ago.

TABLE 3-57. PERCENT PLUTONIUM LEACHED BY EXTRACTANTS (BONDIETTI ET AL., 1975)

	Percent Leached		
Extractant	Humate	Montmorillonite	Kaolinite
10^{-3}M Citrate	0.3	8	11
10^{-3}M DTPA	30	15	20
10^{-2}M Fulvate	5	0.9	3

Bondietti (1974) determined the plutonium Kd for clays separated from a soil (Miami silt loam) and montmorillonite using 5×10^{-3}M calcium solutions at pH 6.5 for two plutonium valence states. The results are shown in Table 3-58. The high adsorption of Pu(VI) on the soil clay, in contrast to or as compared with montmorillonite, indicated that plutonium reduction by clay components must have occurred, since adsorption values similar to the Pu(IV) were obtained. Pu(VI) appeared to adsorb less than Pu(IV).

TABLE 3-58. PLUTONIUM Kd AS A FUNCTION OF OXIDATION STATE (BONDIETTI, 1974)

Material	Initial Oxidation	Kd, ml/g
Soil Clay Fraction	Pu(IV)	$1.0 - 1.7 \times 10^5$
	Pu(VI)	7.5×10^4
Montmorillonite	Pu(IV)	2.1×10^4
	Pu(VI)	2.5×10^2

Relyea and Brown (1975) studied the adsorption-desorption relations of plutonium solutions added to water at pH 2. The ratio of plutonium adsorbed by the soil to that in the equilibrium solution was greater than 99.1. Diffusion of plutonium in four soils was found to be much slower than for exchangeable soil cations.

Volesky and Friedman (1976) used ^{237}Pu to study the adsorption of plutonium on Niagara limestone surfaces (k), and the effect of sodium chloride concentrations on k values. A k is defined as (^{237}Pu activity/ml of solution)/(^{237}Pu activity/cm^2 of limestone), with the dimensions ml/cm^2. The k value is essentially constant until NaCl is 1M in concentration. The k then increases rapidly to 3M NaCl and again becomes constant. As the k value increases, ^{237}Pu is being desorbed from the limestone and re-entering the solution. The desorption may result from the formation of plutonium chloride complexes.

Rai and Serne (1977) used thermodynamic data to develop solid phase-soil solution equilibria diagrams which can be used to estimate plutonium behavior in terrestrial environments. PuO_2 was the most stable phase in the pH and oxygen partial pressure ranges found in soil environments. Plutonium experimental results found in the literature were used to verify empirical predictions, based on the diagrams, of plutonium adsorption on soils.

Migration Results

Field Studies--

Magno et al. (1970), in investigations of radionuclide migration from the Nuclear Fuel Services plant in New York State, estimated that more than 90% of the ^{238}Pu, ^{239}Pu and ^{241}Pu contained in the plant effluent remained in the sediments of the lagoon system.

A series of wells were drilled into the contamination produced by the 1973 leakage of 435,000 liters of high level waste from a Hanford storage tank (Anon., 1973). Core sample analysis showed the relative mobilities of the radionuclides contained in the high pH, high salt solution. Plutonium had migrated the shortest distance from the tank rupture of all the radionuclides in the contaminated sediments.

Emery et al. (1974a, 1974b, 1975) have discussed the plutonium inventory of a 56,657 m^2 reprocessing waste pond at Hanford. The pond has received wastewater since 1944, which included about 1 Ci of $^{239,240}Pu$. It has retained greater than 99% of this plutonium in the upper 20 cm of its sediments even though no water leaves the pond except by evaporation or soil percolation and the mean residence time of the water is only 40 hr (Emery et al., 1974). The plutonium is probably present in a particulate form.

The plutonium resulting from operation of the natural reactor at Oklo 1.8 billion years ago was reported to have remained in the vicinity of the original reactor site (Brookins, 1976).

Bondietti and Reynolds (1975) investigated the species of plutonium found in Oak Ridge seepage water from a solid waste burial ground. Pu(VI) was identified as the main Pu species in the seepage solutions from the burial ground. The implication is that Pu(VI) is more mobile than Pu(IV).

Water infiltration and plutonium migration at Maxey Flats burial grounds were studied by Meyer (1975). A hydrostatic head of 4 to 6 m was found in some trenches, causing lateral and downward migration of leachates. Surficial plutonium migration also had occurred from trench leakage. Above background plutonium concentrations have been detected in onsite and offsite surface soils and stream sediments, in soil cores to 90 cm and in wells 15 to 27 m deep. Other radionuclides accompanying the plutonium included tritium, ^{60}Co, ^{89,90}Sr and ^{134,137}Cs.

Radiological measurements at the Maxey Flats burial site, Kentucky, also have indicated some physical radionuclides transport on particulate matter (Meyer, 1975; Montgomery et al., 1977). The authors mentioned that ^{54}Mn, ^{60}Co, ^{90}Sr, ^{137}Cs, ^{238}Pu and ^{239}Pu were detected in stream sediments, although the water levels were quite low. In E-Series test well measurements, all plutonium within the detection limit was associated with sediment. The authors suggest that this raises a question as to the mechanism of plutonium migration from the disposal trenches.

Laboratory Studies--

Lindenbaum and Westfall (1965) prepared several dilute solutions of colloidal plutonium with citrate to plutonium ratios of 1800 (3.4×10^{-2}M citrate) to 1. The colloid was about 80% ultrafilterable at pH 4.0 and a citrate to plutonium ratio of 1. The cellophane used in the ultrafiltration had a pore size that corresponded to a plutonium hydroxide molecular weight of about 200,000. At pH 10, the citrate to plutonium ratio 1 colloid fell to 65% ultrafilterable and 5% at pH 11. The citrate to plutonium ratio 1800 colloid behaved in a similar fashion falling from 92% ultrafilterable at pH 4 to 72% at pH 11. With no citrate present, the plutonium was about 13% ultrafilterable at pH 4 and fell to near 0% at pH 11. Qualitatively, Zr(IV), Th(IV) and the rare earths may behave in a similar manner, peptizing at higher pH, as suggested by the works of Rhodes (1957). The dispersed polymers are less soil-reactive and should migrate farther through the soil. Hajek (1965) determined that the migration rate in soil, relative to groundwater, was 1/100 and 1/1000 times the rate of groundwater flow for strontium and cesium, respectively. The diffusion velocities of plutonium and americium were 1/10,000 times the transporting solution velocity (Hajek, 1966). The apparent self-diffusion coefficient for plutonium was 4.8×10^{-12} cm^2/sec, so that the average distance diffused in 329,000 years was 10 cm (Hajek, 1966). The 329,000 years was 13.5 half-lives for ^{239}Pu. Relyea (1977) determined the diffusion coefficient for plutonium in the same soil using a quick freeze method developed by Brown et al. (1964). He obtained an apparent plutonium diffusion coefficient of 5×10^{-10} cm^2/sec at 791 hr on the same Burbank loamy sand.

Hajek (1966) reported that plutonium mobility from contaminated soils was low in the Hanford 216-Z-9 covered trench. About 0.1% of the plutonium could be leached with groundwater, but about 7.5% of the resident americium was removed. No further plutonium was leached after a throughput of 13 column volumes of groundwater. At least 3.5% of the plutonium on the soil was removed by 20 column volumes of 1N $NaNO_3$ solution. The leach rate was constant after 20 column volumes. One column volume was equivalent to 61 cm of leaching solution.

The role of microorganisms in the movement of soil plutonium has been under study by Au (1974). He reported that the plutonium discrimination factor was about 4 between agar growth medium at pH 2.5 and Aspergillus spores. The pH 2.5 probably aids in maintaining plutonium mobility. However, the usual discrimination factor between soil and plants, for example, is 10^4 to 10^6 (Francis, 1973). Acid-producing molds that could increase plutonium solubilization were also identified in the soil.

Fried et al. (1974), in their plutonium distribution studies in limestones and basalts, indicated that the adsorption coefficients were dependent on the types and amounts of other ions in solution. At least two chemical forms of plutonium were migrating in neutral solutions. One of these, possibly a polymerized plutonium oxide, migrated ten times faster through rock fissures than the other form.

Jakubick (1975) modeled the migration of plutonium down the soil profile and found that the migration rate of PuO_2 (0.8 cm/yr) was about 100 times faster than plutonium applied to the soil as $Pu(NO_3)_4$.

Nishita et al. (1976) determined the extractability of plutonium from a contaminated soil as a function of pH. The pH influences hydrolysis and precipitation of the plutonium. In the study, 2 g of contaminated soil was agitated in 25 ml of solution, in duplicate, and the pH adjusted with NaOH or HNO_3. The Kd values are given in Table 3-59 for the Aiken clay loam, a kaolinitic soil, at several pH values. It is not clear from the report whether these values are initial or final system pH measurements. The pH values, at the high and low ends of the range especially, usually drift considerably during equilibrations with soils so a final pH measurement is most meaningful. The Kd values are given in Table 3-59 because it should be of little importance as to which direction equilibrium is approached.

TABLE 3-59. Kd VALUES OF ^{238}Pu IN UNTREATED AIKEN CLAY LOAM (NISHITA ET AL., 1976)

pH	^{238}Pu Kd, mg/ℓ	pH	^{238}Pu Kd, mg/ℓ
1.21	430 ± 44	8.54	963 ± 130
2.12	862 ± 33	9.43	512 ± 14
2.56	796 ± 59	10.31	3.02 ± 1.6
4.69	2591 ± 591	11.25	213 ± 5.8
5.55	2347 ± 220	12.22	138 ± 4.8
7.08	3086 ± 19	13.25	207 ± 14

The migration of plutonium and americium in the lithosphere was investigated by Fried et al. (1976). Most of the plutonium and americium were strongly held on tuff, basalt and limestone. Migration rates of 10^{-5} m/m of water flow were measured in one case, and 30 μm/m of water flow for plutonium migration in another instance into limestone. A small amount, less than 35%, of the plutonium appeared to migrate at a rate about 10 times as fast as the rest of the plutonium. This rapidly moving plutonium may be adsorbed on fine mineral particles. Also, the chemical environment can drastically increase the migration rate of plutonium and americium. Even dilute solutions (10^{-4}M) of highly charged ions cause substantial desorption and migration of plutonium and americium adsorbed on rock surfaces.

Relyea and Brown (1975) measured the diffusion coefficients of plutonium in soil and in water by a capillary tube diffusion cell suggested by Brown et al., (1964). The soil diffusion coefficients were measured by contacting cells containing contaminated and uncontaminated soils for a known time interval, freezing instantly with liquid air, and slicing and counting of sections of the untagged soil perpendicular to the diffusion axis. The apparent diffusion coefficients were low compared to normal soil cations, 1.4×10^{-8} cm^2/sec in a sandy soil to less than 5×10^{-11} cm^2/sec in a silt loam. Associated Kd values were 300 to 500 ml/g for the sandy soil and 10,000 ml/g for the silt loam. EDTA and DTPA reduced most Kd values by a factor of up to 100. The aqueous diffusion coefficients varied from 3.1×10^{-7} cm^2/sec in solution extracted from the silt loam to 2.7×10^{-5} cm^2/sec in a solution extracted from the sandy soil.

Fried et al. (1977) reported the upper limits of the relative migration ratios (radionuclide distance moved/water distance moved) of plutonium and americium through rocks to be 100 μm/m and 500 μm/m of water flow, respectively. Using a migration ratio of plutonium of 125 μm/m of water flow, and a water flow of 0.6 km/yr, the plutonium would migrate no more than 12.5 cm/yr. The ^{241}Am moves faster but has a shorter half-life. The authors concluded that deep burial in geological formations would provide effective isolation of actinides from the environment. Several rather large assumptions are contained in this conclusion. One of these assumptions is that the small cores used to obtain the migration data perfectly model a geologic waste repository.

Further work on the rapidly migrating form of plutonium was reported by Friedman et al. (1977). In one case, a HDEHP column was used to remove all polymeric plutonium species before the experiment, and the rapidly moving plutonium was eliminated. In another treatment, the plutonium solution was evaporated repeatedly with HNO_3 with the same experimental results. Thus, the identification of the rapidly moving plutonium form as a polymer was verified.

A model was devised to predict the flow of wastes containing plutonium through rock fissures. The model will be field tested by core drilling a former disposal site at Los Alamos and comparing predicted and actual movement of the actinides through the tuff.

Fried et al. (1977) also studied the retention of Pu(VI) on Los Alamos tuff with a stock solution of plutonium containing 268 μg Pu(VI)/ml. The adsorption spectrum of PuO_2^{+2} at 830 nm was used to verify the purity of the stock solution. A 10 ml tuff cylinder, coated with wax on the exterior, was used at a flow rate of 2 ml/hr. Prior to use, the tuff column was vacuum evacuated under water to ensure saturation. Measured amounts of Pu(VI) were placed on top of the column and allowed to percolate downward. Water was slowly passed down the column to simulate the passage of groundwater. The effluent water was collected in several fractions and analyzed. The value obtained for Pu(VI) migration was 26,500 μm/m of water flow through the tuff. The comparable Pu(IV) migration was 100 μm/m of water flow. After eight free column volumes (2.4 ml/free column volume) passed through the tuff, a switch to 4N HNO_3 rapidly stripped most of the remaining plutonium. A small amount of residual plutonium, evenly distributed in the tuff column, may or may not have been Pu(VI).

Wildung et al. (1973, 1977) have considered the influence of soil microbial processes on the long-term solubility, form and plant availability of the transuranic elements. Diffusible plutonium in soils, usually less than 0.1% of the total plutonium, appeared to be particulates of hydrated oxide but there was evidence of microorganisms affecting the solubility, form and plant availability of transuranics. Plutonium toxicity was a function of plutonium solubility in soil but microorganisms were generally resistant, with toxicity due to radiation effects. Highly resistant bacteria, fungi and actinomycetes were isolated from the soil and shown to transport plutonium into the cell, altering its form to a soluble, negatively-charged complex. The plutonium forms were not well defined, but were dependent on organism type, carbon source and plutonium exposure time during growth.

Summary

In most oxidizing environments, ionic plutonium is expected to be present in solution predominantly as Pu(V) or Pu(VI) (Figures 3-17 and 3-18). With high plutonium concentrations, PuO_2 could be expected as a stable solid phase (Figures 3-15 and 3-16). The plutonium adsorption data indicate that more than one mechanism is operating during reactions with rocks and soils. There is a direct correlation of plutonium adsorption results with soil cation exchange capacities (Thorburn, 1950; Evans, 1956; Rhodes, 1952, 1957a, 1957b; Van Dalen et al., 1975; Glover et al., 1977) indicating that part of the adsorption is due to ion exchange. However, little effect on adsorption was obvious from competing cation concentrations that were very high (Rhodes, 1957a; Mo and Lowman, 1975). Perhaps the principal correlation of plutonium adsorption is with pH (Rhodes, 1952, 1957a, 1957b; Knoll, 1965; Hajek and Knoll, 1966; Knoll, 1969). A relatively rapid soil column breakthrough of plutonium was obtained with a low pH (<1) solution (Knoll, 1965). Strong adsorption occurs over the pH range of from 4 to 8 (Prout, 1958, 1959), but above pH 8 the formation of negative complexes or polymers with low charge densities can cause lowered adsorption (Thorburn, 1950; Rhodes, 1957a; Polzer and Miner, 1977). In addition, plutonium is easily complexed with humic acids (Desai and Ganguly, 1970; Bondietti et al., 1975) and with oxalate (Bensen, 1960), acetate (Rhodes, 1957a) and a large number of phosphorus-bearing organics used in the nuclear fuels reprocessing industry (Knoll, 1969). Complexed plutonium also can result from soil fungal or microbial activities (Wildung et al., 1973, 1977; Au, 1974) all of which result in more mobile plutonium. Even the precipitated or adsorbed plutonium can be readily moved through the aqueous environments in the form of particulates or suspended sediments (Magno et al., 1970; Emery et al., 1974a, 1974b, 1975; Meyer, 1975; Montgomery et al., 1977). If the Eh environment allows it, Pu(IV) can be oxidized to Pu(V) or (VI), with much lower plutonium adsorption values resulting (Bondietti, 1974). The plutonium polymers usually are adsorbed readily, but can migrate more rapidly than soluble plutonium in some instances where the surface charge density is low (Friedman et al., 1977). Much experimental work remains to be done to separate and understand the several reactions mechanisms occurring in plutonium adsorption on rocks or soils. A controlled Eh environment for the adsorption work is important as an experimental condition when an element disproportionates as readily as plutonium.

References

Ames, L. L., Jr. 1974. Characterization of Actinide Bearing Soils: Top Sixty Centimeters of 216-Z-9 Enclosed Trench. BNWL-1812.

Ames, L. L., Jr. 1976. Actinide Occurrences in Sediments Following Ground Disposal of Acid Wastes at 216-Z-9 Covered Trench. BNWL-2117, pp. 39-61.

Andelman, J. B. and T. C. Rozzell. 1970. Plutonium in the Water Environment. I. Characteristics of Aqueous Plutonium. IN: Radionuclides in the Environment. Adv. in Chem. Ser. No. 93. Amer. Chem. Soc., Washington, DC, pp. 118-137.

Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.

Au, F. H. F. 1974. The Role of Soil Microorganisms in the Movement of Plutonium. IN: Dunaway, P. B. and M. G. White (eds). The Dynamics of Plutonium in Desert Environments. NVO-142, pp. 135-141.

Bensen, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Bondietti, E. A. 1974. Adsorption of Pu(IV) and Th(IV) by Soil Colloids. Agronomy Abstracts.

Bondietti, E. A., S. A. Reynolds, and M. H. Shanks. 1975. Interactions of Plutonium with Complexing Substances in Soils and Natural Waters. IAEA-SM-199/51.

Bondietti, E. A. and S. A. Reynolds. 1977. Field and Laboratory Observations on Plutonium Oxidation States. BNWL-2117, pp. 505-533.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brown, D. A., B. E. Fulton and R. E. Phillips. 1964. Ion Diffusion: I, A Quick-Freeze Method for the Measurement of Ion Diffusion in Soil and Clay Systems. Soil Sci. Soc. Amer. Proc. 28:628-632.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. IN: Disposal of Radioactive Wastes Into the Ground. IAEA-SM-93/16, pp. 215-228.

Cherdyntsev, V. V., V. L. Zverev, V. M. Kuptsov, and G. T. Kislitsina. 1968. Plutonium-239 in Nature. Geochemistry International. 5:355-361.

Cleveland, J. M. 1970. The Chemistry of Plutonium. Gordon and Breach Science Publishers.

Crawley, D. T. 1969. Plutonium-Americium Soil Penetration at 234-5 Building Crib Sites. ARH-1278.

Desai, M. V. M. and A. K. Ganguly. 1970. Interaction of Trace Elements with Organic Constituents in the Marine Environment. BARC-488.

Duursma, E. K. and D. Eisma. 1973. Theoretical, Experimental and Field Studies Concerning Reactions of Radioisotopes with Sediments and Suspended Particles of the Sea. Part C: Applications to Field Studies. Netherlands Journal of Sea Research. 6:265-324.

Duursma, E. K. and M. G. Gross. 1971. Marine Sediments and Radioactivity. IN: Radioactivity in the Marine Environment. National Academy of Sciences. pp. 147-160.

Duursma, E. K. and P. Parsi. 1974. Distribution Coefficients of Plutonium Between Sediment and Seawater. IN: Activities of the International Laboratory of Marine Radioactivity. IAEA-163. pp. 94-96.

Emery, R. M., D. C. Klopfer and W. C. Weimer. 1974a. Ecological Behavior of Plutonium and Americium in a Fresh Water Ecosystem. Phase I. Limnological Characterization of Isotopic Distribution. BNWL-1867.

Emery, R. M. and T. R. Garland. 1974b. The Ecological Behavior of Plutonium and Americium in a Fresh Water Ecosystem: Phase II. Implications of Differences in Transuranic Isotopic Ratios. BNWL-1879.

Emery, R. M., D. C. Klopfer, T. R. Garland and W. C. Weimer. 1975. Ecological Behavior of Plutonium and Americium in a Freshwater Pond. BNWL-SA-5346.

Evans, E. J. 1956. Plutonium Retention in Chalk River Soil. CRHP-660.

Francis, C. W. 1973. Plutonium Mobility in Soil and Uptake in Plants: A Review. Journal Environmental Quality. 2:67-70.

Fried, S. M., A. M. Friedman, and L. H. Fuchs. 1973. Retention of Actinide Elements on Soils and Rocks in the Natural Environment. ANL-7996. pp. 6-7.

Fried, S. M., A. M. Friedman, and L. A. Quarterman. 1974. Annual Report on Project AN0115A, Fiscal Year 1974. ANL-8115.

Fried, S., A. M. Friedman, and R. Weeber. 1974. Studies on the Behavior of Plutonium and Americium in the Lithosphere. ANL-8096.

Fried, S., A. M. Friedman, J. J. Hines, R. W. Atcher, L. A. Quarterman and A. Volesky. 1976. The Migration of Plutonium and Americium in the Lithosphere. IN: Actinides in the Environment, Chapter 3. ACS Symposium Series 35, A. Friedman, ed.

Fried, S., A. M. Friedman, J. Hines, G. Schmitz, and M. Wheeler. 1977. Distribution of Plutonium and Americium at an Old Los Alamos Waste Disposal Site. IN: Dynamics of Transuranics in Terrestrial and Aquatic Environments.

Friedman, A. M., S. Fried, J. Hines, and L. Quarterman. 1977. Migration of Pu and Am. BNWL-2117, pp. 73-102.

Fukai, R. and C. N. Murray. 1974. Adsorption and Desorption of Plutonium and Americium in Freshwater - Sediment and Seawater - Sediment Systems. IN: Activities of the International Laboratory of Marine Radioactivity. IAEA-163, pp. 96-103.

Glover, P. A., F. J. Miner, and W. L. Polzer. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. I. Sorption of Plutonium and Americium by Soils. BNWL-2117.

Grebenshchikova, V. I. and Y. P. Davydov. 1961. A Study of the State of Pu(IV) in Dilute Solutions of Nitric Acid. Radiokhimiya. 3:155-164.

Grebenshchikova, V. I. and Y. P. Davydov. 1965. State of Pu(IV) in the Region of pH 1.0-12.0 at a Plutonium Concentration of 2.0×10^{-5}M. Radiokhimiya. 7:191-195.

Hajek, B. F. 1966. Plutonium and Americium Mobility in Soils. BNWL-CC-925.

Hajek, B. F. and K. C. Knoll. 1966. Disposal Characteristics of Plutonium and Americium in a High Salt Acid Waste. BNWL-CC-649.

IAEA. 1975. International Atomic Energy Agency. The Oklo Phenomenon. Proc. Sym., Libreville, 23-27. June 1975.

Jakubick, A. T. 1975. Migration of Plutonium in Natural Soil. IAEA-SM-199/3.

Keller, C. 1971. The Chemistry of the Transuranium Elements. Vol. 3. Kernchemie in Einzeldarstellungen. Verlag Chemie GmbH.

Knoll, K. C. 1965. Reaction of High Salt Aqueous Plus Organic Waste with Soil. BNWL-CC-313.

Knoll, K. C. 1969. Reactions of Organic Wastes in Soils. BNWL-860.

Lindenbaum, A. and W. Westfall. 1965. Colloidal Properties of Plutonium in Dilute Aqueous Solution. Inter. J. App. Radiation and Isotopes. 16:545-553.

Magno, P., T. Reavey, and J. Apidiunakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH/NERHL-70-2.

Meyer, G. L. 1975. Preliminary Data on the Occurrence of Transuranium Nuclides in the Environment at the Radioactive Waste Burial Site. Maxey Flats, KY. IAEA-SM-199/105.

Miner, F. J., P. A. Glover, and H. W. Miller. 1973. Plutonium Behavior in the Soil/Water Environment. RFP-2004-A, pp. 1-3.

Miner, F. J., P. A. Glover, and W. L. Polzer. Plutonium Behavior in the Soil/ Water Environment. I. Sorption of Plutonium by Soils. Agronomy Abstracts. p. 35.

Mo, T. and F. G. Lowman. 1975. Laboratory Experiments on the Transfer Dynamics of Plutonium from Marine Sediments to Seawater and to Marine Organisms. CONF-750503-5.

Montgomery, D. M., H, E. Kolde, and R. L. Blanchard. 1977. Radiological Measurements at the Maxey Flats Radioactive Waste Burial Site 1974-1975. EPA-520/5-76/020.

Nishita, H., M. Hamilton, and A. J. Steen. 1976. Extractability of ^{238}Pu and ^{242}Cm from a Contaminated Soil as a Function of pH and Certain Soil Components. Presented at Meeting of Soil Science Society of America. November 28-December 3. Houston, Texas.

Polzer, W. L. 1971. Solubility of Plutonium in Soil/Water Environments. CONF-710401, pp. 411-430.

Polzer, W. L. and F. J. Miner. 1974. Plutonium Behavior in the Soil/Water Environment. II. Mechanisms of Plutonium Sorption by Soils. Agronomy Abstracts. p. 37.

Polzer, W. L. and F. J. Miner. 1977. Plutonium and Americium Behavior in the Soil/Water Environment. II. The Effect of Selected Chemical and Physical Characteristics of Aqueous Plutonium and Americium on Their Sorption by Soils. BNWL-2117, pp. 255-286.

Price, K. R. 1971. A Critical Review of Biological Accumulation, Discrimination and Uptake of Radionculides Important to Waste Management Practices. BNWL-B-148.

Price, K. R. 1973. A Review of Transuranic Elements in Soils, Plants, and Animals. Journal Environment Quality. 2:62-66.

Price, S. M. and L. L. Ames. 1975. Characterization of Actinide-Bearing Sediments Underlying Liquid Waste Disposal Facilities at Hanford. IAEA-SM-199/87.

Prout, W. E. 1958. Adsorption of Radioactive Wastes by Savannah River Plant Soil. Soil Science. 86:13-17.

Prout, W. E. 1959. Adsorption of Fission Products by Savannah River Plant Soil. DP-394.

Rai, Dhanpat and R. J. Serne. 1977. Plutonium Activities in Soil Solutions and the Stability and Formation of Selected Plutonium Metals. Journal Environmental Quality. 6:89-95.

Relyea, J. F. 1977. The Behavior of Plutonium in Soil. Ph.D. Thesis, University of Arkansas, Fayetteville, AR.

Relyea, J. F. and D. A. Brown. 1975. The Diffusion of Pu-238 in Aqueous and Soil Systems. Agronomy Abstracts. p. 124.

Rhodes, D. W. 1952. Preliminary Studies of Plutonium Adsorption in Hanford Soil. HW-24548.

Rhodes, D. W. 1957a. The Adsorption of Plutonium by Soil. Soil Science. 84:465-471.

Rhodes, D. W. 1957b. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Science Society of America, Proceedings. 21:389-392.

Rozzell, T. C. and J. B. Andelman. 1971. Plutonium in the Water Environment. II. Sorption of Aqueous Plutonium on Silica Surfaces. Advances in Chemistry Series. 106:280-98.

Savannah River Laboratory Quarterly Report Waste Management. April-June 1975. DPST-75-125-2.

Schneider, H. and W. Block. 1968. On the Question of the Capacity of the Rhine for Radioactive Nuclides. Sorption of Radionuclides by Sediments of the Rhine. Gas Gasserfach. 109:1410-15 (in German).

Sheidina, L. D. and E. N. Kovarskaya. 1970. Colloidal State of Pu(IV) in Aqueous Solutions. Sov. Radio. Chem. 12:229-233.

Tamura, T. 1974. Distribution and Characterization of Plutonium in Soils from Nevada Test Site. p. 24-42. IN: P. B. Dunaway and M. G. White (ed.) The Dynamics of Plutonium in Desert Environments. NVO-142.

Tamura, T. 1972. Sorption Phenomena Significant in Radioactive - Waste Disposal. IN: Underground Waste Management and Environmental Implications. T. D. Cook (ed.). Am. Assoc. Petrol. Geol. pp. 318-330.

Tamura, T. 1975. Characterization of Plutonium in Surface Soils from Area 13 of the Nevada Test Site. IN: The Radioecology of Plutonium and Other Transuranics in Desert Environments. M. G. White and P. B. Dunaway (eds.). NVO-153, pp. 27-41.

Tamura, T. 1975. Physical and Chemical Characteristics of Plutonium in Existing Contaminated Soils and Sediments. IAEA-SM-199/52.

Thorburn, R. C. 1950. Absorption on Hanford Soil and Related Soil Properties. HW-15655.

Van Dalen, A., F. DeWitte, and J. Wiskstra. 1975. Distribution Coefficients for Some Radionuclides Between Saline Water and Clays, Sandstones and Other Samples from the Dutch Subsoil. Reactor Centrum Nederland. pp. 75-109.

Volesky, A. F. and A. M. Friedman. 1976. Niagara Limestone Absorption of Plutonium from Salt Solutions. ANL.

Wildung, R. E. and T. R. Garland. 1973. Influence of Soil Microbial Activity on the Uptake and Distribution of Plutonium in the Shoots and Roots of Barley. BNWL-1850, Pt. 2, pp. 22-25.

Wildung, R. E. and T. R. Garland. 1977. The Relationship of Microbial Processes to the Fate and Behavior of Transuranic Elements in Soils and Plants. IN: The Transuranium Elements in the Environment. W. C. Hanson (ed.).

PROMETHIUM

Natural Soil and Rock Distributions

Promethium has not been found to occur naturally in soils and rocks.

Brief Chemistry

There are 16 known radioactive isotopes and isomers of promethium with mass numbers from 141 to 154 and half-lives ranging from 34 sec to 17.7 years (Lavrukhina and Pozdnyakov, 1970). Promethium-147 (half-life 2.5 years) is the only promethium isotope obtained in large amounts from ^{235}U fissioning by thermal neutrons, and is present in fuel reprocessing fission products.

Promethium is a lanthanide and like most lanthanides exists in a trivalent state. Only the (III) oxidation state of promethium is stable in aqueous soil solutions. Starik and Lambert (1958) studied the state of micro-amounts of promethium in aqueous solutions at different pH values by ultrafiltration and centrifugation. The results showed that promethium was present as Pm^{+3} at pH $\leq$ 3. With an increase in pH, hydrolysis products gradually accumulate as multiply-charged aggregates. After a maximum is reached at pH of about 7, the charged aggregates begin to flocculate. At higher pH values, the aggregates become neutral or negatively charged. Electrophoteric measurements showed that from pH 5.3 to 6.7, the bulk of the polynuclear particles was positively charged. At pH 9, no mobility is seen, indicating neutrally charged particles. At pH 5 to 8, no promethium can be centrifuged, indicating a colloid in solution. At pH 9, uncharged forms such as $[Pm(OH)_x(NO_3)_{3-x}]^0$ predominate (Starik et al., 1959).

Solid Phase and Soil Solution Equilibria

Promethium forms crystalline compounds with F^-, Cl^-, Br^-, I, OH^-, PO_4^{3-}, AsO_4^{3-}, BO_3^{3-}, CrO_4, CrO_3, MoO_4^{2-}, WO_4^{2-}, VO_4^{3-}, ScO_3^{3-} (Lavrukhina and Pozdnyakov, 1970; Wheelwright, 1973). However, the thermodynamic data are available for $Pm(OH)_3$ (solid) (Sillen and Martell, 1964) and Pm_2O_3 (Pourbaix, 1966). It is evident that $Pm(OH)_3$ is more stable than Pm_2O_3 (Figure 3-19). The Pm^{3+} activity in equilibrium with $Pm(OH)_3$ decreases a thousand-fold with a one unit increase in pH.

Promethium is a lanthanide and like most lanthanides exists in a trivalent state (Pm^{3+}). No data were found on solution species of promethium except for $PmNO_3^{2+}$ ($Pm^{3+} + NO_3^- \rightleftarrows PmNO_3^{2+}$ log K° at I = 1 is 2.48) (Lavrukhina and Pozdnyakov, 1970). The solution species is probably predominantly Pm^{3+}, much like europium. If it assumed that promethium does not form any other complexes, then the concentration of promethium in solution will be governed mainly by Pm^{3+}. Under these conditions, ion exchange can be an important promethium removal mechanism in acidic environments and at trace promethium concentrations.

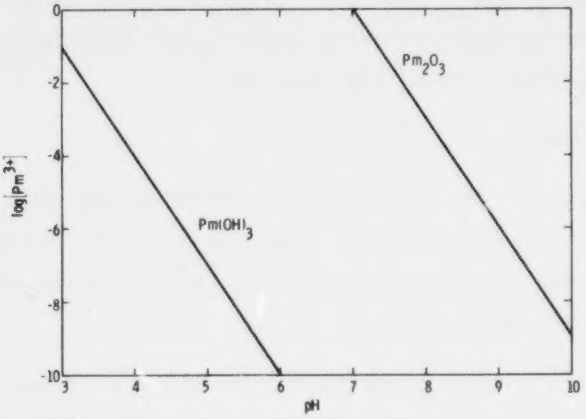

Figure 3-19. The relative stability of various promethium solids.

Experimental Adsorption Results

Bensen (1960) reported the complete uptake of promethium and other trivalent rare earths at pH > 6. Promethium behavior in soil systems was said to be identical to cerium behavior. The uptake of promethium is nearly complete and unaffected by 0.5M alkali metal and 0.25M alkaline earth metal cations at above pH 7. Below pH 3, the adsorption of all rare earths including promethium is depressed similarly by accompanying salts. The results indicate that promethium and other rare earths are ionic species below pH 3, and begin to precipitate as charged polymers above pH 3. Bensen (1960) also reported that the species and amount of accompanying anion affect promethium adsorption by soils. Citrate, acetate and carbonate ions were found to inhibit rare earth adsorption on soils. This was attributed to formation of complex ion species. Chloride and nitrate ions had no appreciable effect on adsorption, and sulfate had very little effect.

Migration Results

Field Studies--

Magno et al. (1970) investigated migrating radionuclides from the Nuclear Fuel Services plant in western New York State. They estimated from analytical data that greater than 90% of the ^{147}Pm discharged from the plant was deposited by sedimentation in the lagoon system. These results imply that most of the promethium was a precipitate, probably $Pm(OH)_3$, or adsorbed on other solids in the water that settled out in the lagoons.

Laboratory Studies--

Ames (1960) reported the removal of promethium during a replacement reaction of calcite with phosphate in solution. The promethium was finally immobilized in apatite, $Ca_5(PO_4)_3OH$, where 2 Ca^{2+} are replaced by a Pm^{3+} and Na^+ or some other univalent cation.

Schulz (1965) classified promethium with other rare earths as immobile in soils due to either very strong adsorption by clay particles or present as insoluble hydroxide.

Summary

Low concentrations of promethium are expected in equilibrium with $Pm(OH)_3$ in slightly acidic to slightly alkaline conditions (Figure 3-9) so that $Pm(OH)_3$ precipitation may control promethium concentrations in soil and sediment solutions. Promethium, like europium, would be expected to be ion exchangeable below the concentration required for $Pm(OH)_3$ precipitation. Only limited data are available on promethium adsorption on soils and sediments, but these data tend to support the above predictions.

The removal of promethium is nearly complete on soils and rocks above pH 6 (Bensen, 1960). The effect of competing cations on promethium adsorption above pH 7 is minimal. Below pH 3, the adsorption of all rare earths including promethium are similarly depressed by competing salts. Charged polymers can form under the proper conditions during $Pm(OH)_3$ precipitation (Starik et al., 1959; Bensen, 1960). Citrate, acetate and carbonate ions inhibited rare earth adsorption on soils, probably due to the formation of complex ion species. Over 90% of the promethium discharged to a lagoon system remained in the lagoon (Magno et al., 1970) as strongly adsorbed on clay particles or present as an insoluble hydroxide (Schulz, 1965). Promethium can be removed from solution during replacement reactions (Ames, 1960).

References

Ames, L. L., Jr. 1960. Some Cation Substitutions During the Formation of Phosphorite from Calcite, Economic Geology. 55:354-362.

Benson, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Lavrukhina, A. K. and A. A. Pozdnyakov. 1970. Analytical Chemistry of Technetium, Promethium, Astatine and Francium. Translated by R. Kondor. Ann Arbor - Humphrey Science Publishers.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, England.

Schultz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Starik, I. E., N. I. Ampelogova, F. L. Ginzburg, M. S. Lambert, I. A. Skulskii, and V. N. Shchebetkovskii. 1959. On the Molecular State of Ultra-Small Quantities of Radioelements in Solutions. Radiokhimiya. 1:370-378 (in Russian).

Starik, I. E. and M. S. Lambert. 1958. State of Microquantities of Promethium in Aqueous Solutions. ZhNKh. 3:136.

Wheelright, E. J. 1973. Promethium Technology. Am. Nucl. Soc. Publication.

RADIUM

Natural Soil and Rock Distributions

The radium content of various igneous and sedimentary rocks is given in Table 3-60. Vinogradov (1959) reported that the radium content of soils ranged from 0.5×10^{-6} to 1.1×10^{-6} ppm. The small amount of radium present in soils has become separated from parent thorium and uranium during rock weathering processes, and most closely follows barium. The radium content of igneous rocks increases by 100 times from ultra-basic to granitic rocks. The radium content of most sedimentary rocks is about the same as that for granites.

TABLE 3-60. AVERAGE RADIUM CONTENT OF VARIOUS ROCK TYPES

Rock Type	Ra, ppm	Reference
Ultrabasic Igneous	0.009×10^{-6}	Davis, 1947
Basic Igneous	0.6×10^{-6}	Evans et al., 1942
Intermediate, Igneous	0.917×10^{-6}	Senftle and Keevil, 1947
Granitic Igneous	1.395×10^{-6}	Senftle and Keevil, 1947
Sandstones	0.71×10^{-6}	Bell et al., 1940
Shales	1.08×10^{-6}	Bell et al., 1940
Limestones	0.42×10^{-6}	Evans and Goodman, 1941

Brief Chemistry

There are 16 isotopes of radium from ^{213}Ra to ^{230}Ra with no ^{218}Ra or ^{229}Ra. All of the isotopes of radium are unstable, and all of the naturally-occurring radium isotopes occur in the thorium decay series (^{228}Ra, ^{224}Ra), the ^{238}U-radium decay series (^{226}Ra), and the ^{235}U-actinium decay series (^{223}Ra) (Vdovenko and Dubasov, 1973). Radium radionuclide data are given in Table 3-61. All are alpha emitters except ^{228}Ra which is a beta emitter. With the present uranium fuel cycle and the much longer half-life, only the ^{226}Ra isotope is of long-term concern in waste disposal. If future energy production includes thorium fuels, then ^{228}Ra also must be included in waste disposal management plans.

TABLE 3-61. RADIUM RADIONUCLIDE DATA (VDOVENKO AND DUBASOV, 1973)

Isotope	Half-Life	Decay Mode
^{223}Ra	11.43 days	α
^{224}Ra	3.64 days	α
^{225}Ra	14.8 days	β^-
^{226}Ra	1622 years	α
^{228}Ra	5.77 ± 0.02 years	β^-

Radium is a homolog of the alkaline-earth elements, with a (II) oxidation state. The radius of the +2 radium ion is 1.52 Å compared to 1.43 Å for Ba^{+2}. The compounds formed by radium and their solubilities are similar to barium. For example, the solubility product of radium sulfate is 4.25×10^{-11} at 25°C (Vdovenko and Dubasov, 1973) and the solubility product of barium sulfate is 1.08×10^{-10} at 25°C (Weast, 1976). Metallic radium dissolves in water with the evolution of hydrogen and the formation of readily soluble $Ra(OH)_2$. Of the alkaline-earth metal cations, Ra^{+2} shows the least tendency for complex formation, although 1:1 complexes with citric, tartaric, succinic and several other acids were detected at pH 7.2 to 7.4 by Schubert et al. (1950). It may be assumed that Ra^{+2} is not hydrolyzed in aqueous solutions, in an analogy with Ba^{+2}, although there is no specific literature on the subject.

Solid Phase and Solution Equilibria

The thermodynamic data for radium compounds are available only for radium nitrate, chloride, iodate and sulfate (Parker et al., 1971). However, all of the compounds except sulfate are very soluble. Therefore, solid phase diagrams are not presented for radium compounds. The solubility product for $RaSO_4$ is $10^{-10.37}$ compared to $10^{-9.96}$ for $BaSO_4$.

No thermodynamic data were located for radium hydrolysis or complex ion species. It is expected the radium will behave in the soil solution much like strontium does. The species Ra^{2+} is expected to be the most important over the normal soil pH range from 4 to 8.

Experimental Adsorption Results

Stead (1964) gave a radium Kd value of 6700 ml/g for NTS tuff. Arnold and Crouse (1965) ran batch adsorption tests on some exchange materials that included the natural zeolites, clinoptilolite and chabazite, as represented by a pelletized molecular sieve (AW-500) and barite (barytes), a natural $BaSO_4$.

The results of the adsorption tests were recomputed as distribution coefficients or Kd values. The solution was a lime-neutralized waste that contained 4100 pCi ^{226}Ra/l, 500 mg/l Ca^{+2}, 80 mg/l Mg^{+2}, 1000 mg/l Na^{+}, 2500 mg/l SO_4^{-2} and 900 mg/l Cl^{-} at pH 7.7. The radium Kd values are given in Table 3-62.

TABLE 3-62. RADIUM Kd VALUES FROM LIME-NEUTRALIZED WASTE; 1.25 g EXCHANGER/l OF WASTE (ARNOLD AND CROUSE, 1965)

Exchanger	Mesh Size	Exchanger Loading, pCi/g	Kd,ml/g
Clinoptilolite	20-50	2650	646
Chabazite	20-50	2900	707
Barite	20-50	2000	490

R. J. Serne of PNL, 1974, used soils from Utah and simulated river water to determine radium distribution coefficients. The soils were pre-equilibrated by four washings with the simulated river water composition shown in Table 3-63 minus the $^{226}RaCl_2$. The fifth solution contained the ^{226}Ra as well as the other constituents, and was used for the radium Kd determinations. The Kd values were determined in triplicate to allow measurement of precision. The Utah soils contained 2 to 5% calcite, with quartz and feldspar constituting the bulk of these sandy, arid soils. Minor constituents included hydromica and a small amount of a smectite clay. The radium Kd results are listed in Table 3-64. The Kd correlated with the cation exchange capacities of the soils.

TABLE 3-63. SIMULATED RIVER WATER COMPOSITION (SERNE, 1974)

Constituent	Added as-	mg/l
Ca	$CaSO_4 \cdot 2H_2O$, $CaCl_2$	82
Mg	$MgSO_4$	26
Na	NaCl	75
K	KCl	3.4
HCO_3	$NaHCO_3$	171
SO_4	$CaSO_4 \cdot 2H_2O$, $MgSO_4$	246
Cl	$CaCl_2$, NaCl, KCl	57
U	UO_3	1
Ra	$RaCl_2$ in HCl solution	7 µg/l

TABLE 3-64. RADIUM DISTRIBUTION COEFFICIENTS WITH THE SOLUTION OF TABLE 3-63 (SERNE, 1974)

Soil	Final pH	Kd, ml/g
I	7.9 7.9 8.0	354 ± 15
II	7.6 7.7 7.6	289 ± 7
III	7.8 7.9 7.8	467 ± 15
IV	7.8 7.6 7.8	214 ± 15

Migration Results

Field Studies--

Granger et al. (1961) and Granger (1963) showed that radium had migrated out of Ambrosia Lake, New Mexico, uranium ores and had been partly reconcentrated in barite ($BaSO_4$) and cryptomelane ($KMn^{2+}Mn^{4+}{}_{7.25}O_{16} \cdot H_2O$) found in and near some of the ore bodies. The $^{226}Ra^{2+}$ occurred in the Ba^{2+} position in barite and the Mn^{2+} position in cryptomelane. The high concentrations of ^{226}Ra were not associated with parent uranium, which is good evidence for the recent migration of radium. The strongly to weakly radioactive cryptomelane partially replaced mudstone that occurred near the ore bodies and was relatively low in uranium content and enriched in lead. This suggests that the lead is radiogenic and has also migrated with the ^{226}Ra. The mechanism involved in reconcentration of the ^{226}Ra is the substitution of $^{226}Ra^{2+}$ for the chemically very similar Ba^{2+} in barite and Mn^{2+} in cryptomelane. Analyses of the outer 5 to 10 cm of mudstone layers near ore disclosed anomalously high radioactivity coupled with an abnormally high lead content. Within mudstone layers, however, the radioactivity was essentially in balance with the uranium content, and the lead content was low.

Hansen and Huntington (1969) determined radium and thorium distributions in a series of morainal soils in Bench Valley, California. Thorium accumulated immediately beneath horizons containing a high amount of organic material. The thorium apparently migrated as organic complexes. Radium was distributed with the uranium in the high organic layers.

The ground and surface water sampling and analyses for radium given by Wruble et al. (1964) and Kaufmann et al. (1975, 1976) for waters of the Colorado Basin and Grants area, New Mexico, respectively, also illustrate the tendency of the radium daughter to become separated from uranium due initially to uranium mining and milling operations, and to continue migrating due to inherent geochemical differences between uranium and radium.

Laboratory Studies --

Several reports have been concerned with the leaching of ^{226}Ra from uranium recovery process tailings and wastes (Whitman and Porter, 1958; Anonymous, 1960; Feldman, 1961), and other authors have shown that radium can be leached from stream sediments, minerals and uranium mill wastes (Starik and Polevaya, 1958; Starik and Lazerev, 1960). The factors that influence leachability of ^{226}Ra from uranium mill waste solids and river sediments were investigated by Shearer (1962) and Shearer and Lee (1964). Less than 1.5 wt% of the river sediments and mill waste solids were greater than plus 20 mesh size and less than 30 wt% were minus 140 mesh in particle size. The amounts of radium leached with distilled water versus time showed that essentially no radium was leached after 15 min. Diffusion of radium from the interior of the particles was relatively insignificant. By varying the liquid to solid ratio in distilled water-solid leaching equilibria, it was shown that the ratio affects the amount of radium leached. The largest ratio effect was shown with leaching of the acid leach process tailings, less with alkaline leach process tailings and the least from river sediments. It was demonstrated that sulfate was present in the waste solids and that the sulfate was easily solubilized. Trace amounts of barium present led to precipitation of $BaSO_4$ and the coprecipitation of $RaSO_4$. If radium was added prior to the solids-distilled water equilibria, it too was removed from solution by coprecipitation with $BaSO_4$. One-hundredth molar solutions were used in leaching equilibria (100 ml/g river sediment) to determine effects on radium leaching. $MgCl_2$, KCl, NaCl, HCl and water solutions all leached less than 1 μμg of radium while $CaCl_2$ leached 1.2 μμg Ra, $SrCl_2$ 6.3 μμg Ra and $BaCl_2$ 30 μμRa. Apparently the radium on river sediments is in the form of Ra^{+2} and is exchangeable.

Havlik et al. (1968a) investigated the leaching of ^{226}Ra from uranium mill solids and uranium ores. The first report concerned the effects of pH on leaching rates. The authors found, like Shearer and Lee (1964), that equilibrium leaching was rapidly accomplished in 15 to 30 min. Homogenized uranium ores (540 pCi Ra/g and 85 pCi Ra/g) and milling tailings (14 pCi Ra/g) were shaken for varying lengths of time as a 3g solid/30 ml solution ratio. The pH was modified from 1 to 14 with hydrochloric acid, boric acid and sodium hydroxide. At pH 1, 22% of the ^{226}Ra was liberated. At pH 9, the amount leached had decreased to 2.8%. At pH 13, the amount of leached ^{226}Ra increased to 5%.

The second report by Havlik et al. (1968b) studied the leaching of radium from the same solids as affected by leaching solution composition in addition to acidity. Unlike the leaching results of Shearer and Lee (1964), Havlik et al. found that the largest concentrations of radium were leached by 1N KCl and 1N NaCl solutions. $BaCl_2$, $SrCl_2$ and $CaCl_2$ also were used, but with much less radium liberated. The 1N KCl leached 100% of the radium in mill tailings and NaCl, 95%. Uranium ore leaching results were lower, showing 22% and 31% leached by KCl and 14% and 17% leached by NaCl. In all cases, the one normal salt solutions removed more radium than ten normal salt solutions.

Summary

Radium is present as Ra^{2+} over the normal soil pH range (4 to 8) and shows little tendency to form complex species (Schubert et al., 1950). Radium would be expected to substitute for other divalent cations during replacement or precipitation reactions (Granger et al., 1961; Granger, 1963). A direct correlation of cation exchange capacity with adsorption (Arnold and Crouse, 1965; Serne, 1974) and leaching studies with different types of competing cations (Starik and Polevaya, 1958; Starik and Lazerev, 1960; Shearer, 1962; Shearer and Lee, 1964; Havlik et al., 1968b) suggests that an important reaction mechanism for radium adsorption is cation exchange. Radium could be expected to migrate in much the same manner as strontium.

References

Anonymous. 1960. January, 1960. Summary Report on I. The Control of Radium and Thorium in the Uranium Milling Industry, II. Radium-226 Analysis Principles, Interference and Practice, III. Current Winchester Laboratory Projects. WIN-112.

Arnold, W. D. and D. J. Crouse. 1965. Radium Removal from Uranium Mill Effluents with Inorganic Ion Exchangers. I&EC Process Design and Development. 4:335-337.

Bell, K. G., C. Goodman and W. L. Whitehead. 1940. Radioactivity of Sedimentary Rocks and Associated Petroleum. Bull. Am. Assoc. Petroleum Geol. 24:1529.

Butler, J. N. 1964. Ionic Equilibrium. Addison-Wesley, Reading, MA. pp. 180-183.

Davis, G. L. 1947. Radium Content of Ultramafic Igneous Rocks. I. Laboratory Investigation. Am. J. Sci. 245:677.

Evans, R. D. and C. Goodman. 1941. Radioactivity of Rocks. Bull. Geol. Soc. Am. 52:459.

Evans, R. D., C. Goodman, N. B. Keevil. 1942. Radioactivity: The Earth's Heat and Geological Age Measurements. IN: Handbook of Physical Constants. Geol. Soc. Am. Special Papers 36, Sec. 18, p. 267.

Feldman, M. H. 1961. Summary Report, 1959-1961, Winchester Laboratory, Winchester, Massachusetts and Grand Junction, Colorado. WIN-125.

Granger, H. C. 1963. Radium Migration and Its Effect on the Apparent Age of Uranium Deposits at Ambrosia Lake, New Mexico. U.S. Geol. Survey Prof. Paper 475-B, pp. B-60-B-63.

Granger, H. C., E. S. Santos, B. G. Dean and F. B. Moore. 1961. Sandstone-Type Uranium Deposits at Ambrosia Lake, New Mexico - an Interim Report. Econ. Geol., vol. 56, no. 7, pp. 1179-1209.

Hansen, R. O. and G. L. Huntington. 1969. Thorium Movements in Morainal Soils of the High Sierra, California. Soil Science. 108:257-265.

Havlik, B., J. Grafova, and B. Nycova. 1968a. Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - I. Health Physics. 14:417-422.

Havlik, B., B. Nycova, and J. Grafova. 1968b. Radium-226 Liberation from Uranium Ore Processing Mill Waste Solids and Uranium Rocks into Surface Streams - II. Health Physics. 14:423-430.

Kaufmann, R. F., G. G. Eadie and C. R. Russell. 1975. Summary of Ground Water Quality Impacts of Uranium Mining and Milling in the Grants Mineral Belt, New Mexico. U.S.E.P.A., Off. Rad. Prog.-Las Vegas Facility. Tech. Note ORP/LV-75-4.71 p.

Kaufmann, R. F., G. G. Eadie and C. R. Russell. 1976. Effects of Uranium Mining and Milling on Ground Water in the Grants Mineral Belt, New Mexico. Ground Water. 14(5):296-308.

Parker, V. B., D. D. Wagman, and W. H. Evans. 1971. Selected Values of Chemical Thermodynamic Properties. U.S. Department of Commerce. NBS Technical Note 270-6.

Schubert, A. J., E. R. Russell, and L. S. Myers. 1950. Dissociation Constants of Radium Inorganic Acid Complexes Measured by Ion Exchange. J. Biol. Chem. 185:387-398.

Senftle, F. E. and N. B. Keevil. 1947. Thorium-Uranium Ratios in the Theory of Genesis of Lead Ores. Trans. Am. Geophys. Union. 28:732.

Shearer, S. D., Jr. 1962. The Leachability of Radium-226 from Uranium Mill Solids and River Sediments. Thesis. Univ. Wisconsin.

Shearer, S. D., Jr. and G. F. Lee. 1964. Leachability of Radium-226 from Uranium Mill Solids and River Sediments. Health Physics. 10:217-227.

Starik, I. E. and K. F. Lazarev. 1960. Effect of Crushing of Minerals on the Extraction of Radioactive Elements. Radiokhimiya. II:749-752.

Starik, I. E. and N. I. Polevaya. 1958. The Leachability of ThX and Rd Th from Minerals. AEC-tr-4208, pp. 108.

Stead, F. W. 1964. Distribution in Groundwater of Radionuclides from Underground Nuclear Explosions. IN: Proc. Third Plowshare Symp. Engineering with Nuclear Explosives. April 21-23, 1964. TID-7695, p. 127-138.

Vdovenko, V. M. and Yu. V. Dubasov. 1973. Analytical Chemistry of Radium. Israel Program for Scientific Translations.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau.

Weast, R. C. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co.

Whitman, A. and E. S. Porter. 1958. Chemical Stream Pollution from Uranium Mills. WIN-99.

Wruble, D. T., S. D. Shearer, D. E. Rushing and C. E. Sponagle. 1964. Radioactivity in Waters and Sediments of the Colorado River Basin, 1950-1963. Rad. Health Data, 5(11):557-567.

RUTHENIUM

Natural Soil and Rock Distributions

Few data on natural distribution of ruthenium are available. Data available on ruthenium in rock-forming minerals are listed in Table 3-65. Platinum group metals, including ruthenium, are known to be concentrated in chromite; but these are older analytical values and may be much higher than modern neutron activation ruthenium analyses. There are no ruthenium data on sandstones and limestones. However, the ruthenium contents are probably very low. The meager data on ruthenium content of shales are given in Table 3-66. To put the ppb values into perspective, 100 ppb amounts to 1 x 10^{-7} g of ruthenium per gram of rock or mineral. The behavior and distribution of natural ruthenium during weathering processes is largely unknown.

TABLE 3-65. ABUNDANCES OF RUTHENIUM IN IGNEOUS ROCKS AND ROCK-FORMING MINERALS IN ppm

Mineral	Ru, ppb	Reference
Olivine	10	Noddack and Noddack, 1931
Chromite, Norway	500	Goldschmidt and Peters, 1932
Chromite, Texas	500	Goldschmidt and Peters, 1932
Chromite, Penn.	500	Goldschmidt and Peters, 1932
Columbite, Norway	10	Noddack and Noddack, 1931
Ilmenite	4	Noddack and Noddack, 1931
Rutile	10	Noddack and Noddack, 1931
Tantalite	2	Noddack and Noddack, 1931
Dunite, Russia	2-30 (5 average)	Razin et al., 1965
Dunite, Russia	3-6 (4.5 average)	Razin et al., 1965
Apodunite, Russia	0.9-4 (2.2 average)	Razin et al., 1965
Mica shonkinite	0.5	Razin et al., 1965

TABLE 3-66. RUTHENIUM CONTENTS OF SHALES

Shale	Ru, ppb	Reference
Kupferschiefer, Mansfeld, Germany	3	Noddack, 1936
Black Shale (3)	60 80 40	Tischendorf, 1959
Bleached Shale (3)	40 5 20	Tischendorf, 1959

Brief Chemistry

The 16 isotopes of ruthenium include the radioactive fission products ^{93}Ru, ^{94}Ru, ^{95}Ru, ^{97}Ru, ^{103}Ru, ^{105}Ru, ^{106}Ru, ^{107}Ru and ^{108}Ru. The natural, stable ruthenium isotopes and their abundance are shown in Table 3-67.

TABLE 3-67. ATOMIC PERCENTAGES OF STABLE RUTHENIUM ISOTOPES (HEATH, 1976)

	96	98	99	100	101	102	104
Atom %	5.51	1.87	12.72	12.62	17.07	31.61	18.58

Ruthenium-103 with a 39.6-day half-life and ^{106}Ru with a 367-day half-life are the only radioisotopes of ruthenium that persist long enough to be of concern in waste disposal.

Ruthenium exhibits several oxidation states varying from Ru(-II) to Ru(VIII), with Ru(III) and Ru(IV) the most common oxidation states in aqueous solutions. Ru(II) is less common. For ruthenium, there is little evidence for simple aquo ions. Nearly all aqueous solutions, whatever the anion, may be considered to contain complex ions (Cotton and Wilkinson, 1962). Ru(II), for example, is known to form a unique series of nitrosyl complexes, nitric oxide complexes, ammonia and sulfur complexes, carbonyl complexes, etc.

In an alkaline medium, Ru(IV) forms the insoluble hydrated oxide $RuO_2 \cdot XH_2O$ which does not tend to be reduced to the trivalent state. Ruthenium (III) hydroxide is readily oxidized in air to Ru(IV) (Ginzburg et al., 1975). Ruthenium exists in nitric acid solutions either as the Ru(III) nitrosonitrates

$[RuNO(NO_3)_n(H_2O)_{5-3}]^{3-n}$ or $[RuNO(NO_3)_{5-n-m}(OH)_m \cdot (H_2O)_n]^{p-}$, or as the polymeric Ru(IV) aquohydroxo cations $[Ru(OH)_x(H_2O)_{6-x}]\ (NO_3)_{4-x}$ (Ginzburg et al., 1975). Thus, from acidic nitrate solutions, which are the usual form of fuel reprocessing wastes, ruthenium solutions may be obtained that contain cationic, anionic and neutral complexes. Hence, the chemical forms of the ruthenium in a given media are a product of the chemical history of that media.

Solid Phase and Solution Equilibria

Ruthenium is generally present in association with platinum group metals. The abundance of ruthenium in various rocks and soil forming minerals is summarized in Tables 3-60 and 3-61. Ruthenium also forms discrete solid compounds such as RuO_2, RuO_4, $Ru(OH)_3$, $Ru(OH)_4$, $RuCl_3$, and RuS_2. The relative stability of the discrete solids in oxidizing conditions ($pO_{2(g)}$ = 0.68 atm) is given in Figure 3-20. The thermodynamic data for RuO_2 and RuO_4 were obtained from Wagman et al. (1969). The data for $Ru(OH)_3$ and $Ru(OH)_4$ were selected from Sillen and Martell (1964). The solids in increasing order of stability for the conditions outlined in Figure 3-20 are: $Ru(OH)_3$, RuO_4, $Ru(OH)_4$, and RuO_2 (amorphous, hydrated). $RuCl_3$ and RuS_2 do not appear in Figure 3-20 because they are too soluble and fall beyond the boundaries of the figure. From Figure 3-20 it can be ascertained that RuO_2 (amorphous, hydrated) would be most stable over the pH range and up to reducing environments equivalent to pO_2 of 50. In extremely reducing conditions (pO_2 = 80) where H_2S (aq) would be the most stable sulfur species, RuS_2 would maintain lower activities than RuO_2 and hence would be the most stable.

The activity of various solution complexes of ruthenium in equilibrium with RuO_2 (amorphous, hydrated) in oxidizing (pO_2 0.68) and other conditions spelled out in the graph are given in Figure 3-21. The thermodynamic data used to construct Figure 3-21 were selected from several sources including Sillen and Martell (1964) for $RuOH^{3+}$, Ru^{4+} and Ru^{3+}, Baes and Mesmer (1976) for $RuO_4(OH)^-$, and Wagman et al. (1969) for the remaining species. Baes and Mesmer (1976) indicate that the thermodynamic data on ruthenium complexes are either not available or is not very accurate. However, it was decided to construct Figure 3-21 using the existing data to estimate the nature of the species that may be present in solution.

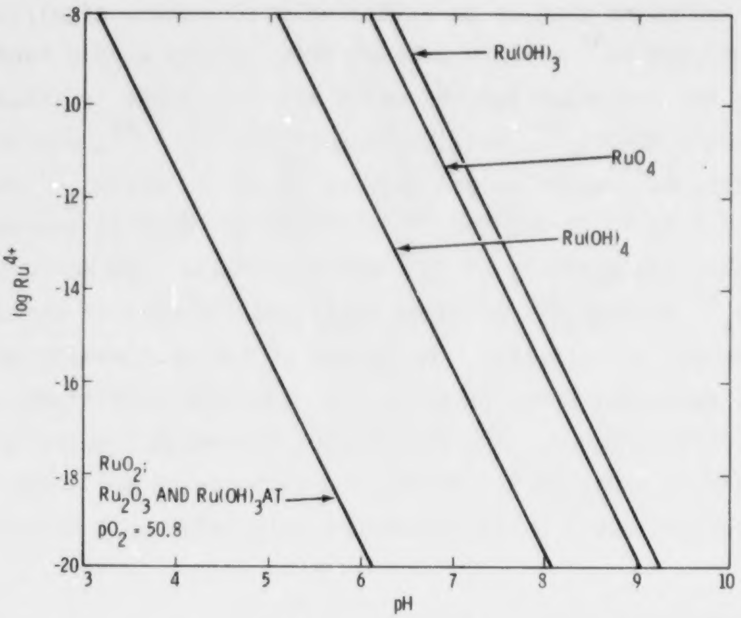

Figure 3-20. The relative stability of various ruthenium solids in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm], $pCl^- = pSO_4^{2-} = 2.5$ and $pH_2S = 3.0$.

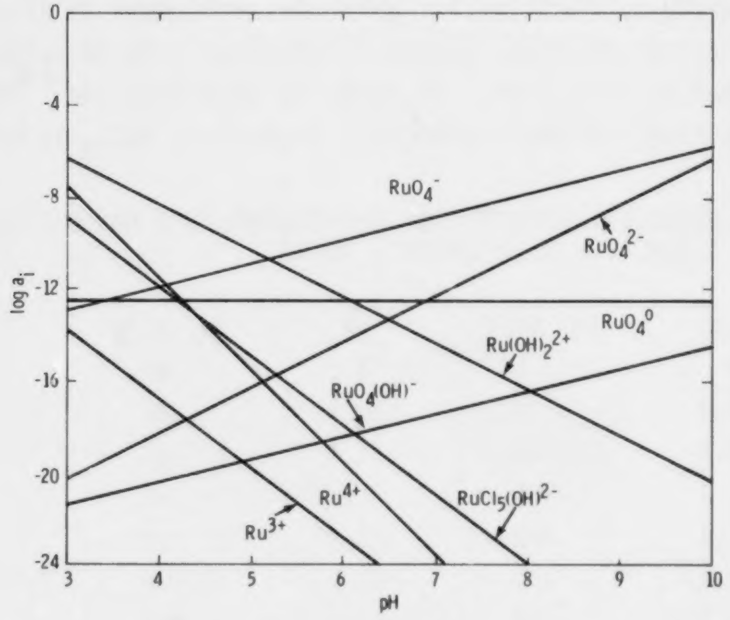

Figure 3-21. The activity of various ruthenium species in equilibrium with RuO_2 (amorphous hydrate) in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm], pCl^- = 2.5.

Figure 3-21 indicates that in an oxidizing environment, significant activity of uncomplexed Ru^{4+} will be present only in very acidic conditions (pH <2). Some of the ruthenium species which may be present in solution are RuO_4^-, RuO_4^{2-}, RuO_4°, $Ru(OH)_2^{2+}$, $RuO_4(OH)^-$, $RuCl_5(OH)^{2-}$, Ru^{4+}, and Ru^{3+}. Among these species, Ru^{4+} would be predominant in pH <2, $Ru(OH)_2^{2+}$ in pH 2 to 5.2, RuO_4^- in pH 5.2 to 10.5, and RuO_4^{2-} in pH >10.5. With an increase in reducing conditions, the activity of Ru^{3+} would increase, the activity of RuO_4°, RuO_4^-, RuO_4^{2-} and RuO_4OH^- would decrease and the rest of the species would remain unchanged in activity. The nature of the predominant solution species is highly dependent upon the oxidation-reduction conditions, as is the most stable solid compound. The predominant ruthenium species are cationic below pH 5 and anionic above pH 5. Hence, ion exchange on soils and rocks, mainly cation exchange, would be of importance only below pH 5 under these conditions.

Experimental Adsorption Results

Rhodes (1957) reported the variation in ^{106}Ru distribution coefficients with solution pH on a typical Hanford subsoil. The soil had a cation exchange capacity of 5 meq/100 g, 2 wt% calcium carbonate, with about 2% clays of mainly montmorillonite and lesser amounts of chlorite. The Kd values for ^{106}Ru are presented in Table 3-68. It should be noted that the ^{106}Ru was obtained from Oak Ridge National Laboratory, probably as $RuCl_3$ in HCl solution.

TABLE 3-68. RUTHENIUM DISTRIBUTION COEFFICIENTS ON A HANFORD SOIL AS A FUNCTION OF pH (RHODES, 1957)

pH	Kd, ml/g	pH	Kd, ml/g
0	0	9.2	40
1.3	0	10.1	39
2.6	26	10.4	44
4.7	101	11.0	92
6.6	752	11.3	27
7.4	460	13.0	101
8.5	274	14.0	752

The soil adsorption of Ru^{+3} in a chloride medium cannot be similar to the adsorption of the nitro- and nitrato complexes of nitrosylruthenium normally present in acidic nitrate waste solutions. Rhodes and Nelson (1957) make this same point when they discuss the soil adsorption of ruthenium present in uranium recovery plant waste. Sampling of groundwater beneath a discontinued disposal facility showed that the concentration of ^{106}Ru remained constant for several months. This indicated little adsorption after the initial breakthrough of ^{106}Ru. Klechkovsky (1956) also investigated ^{106}Ru adsorption on soils but did not specify the type of ruthenium or soils used.

Wilding and Rhodes (1963) reported that the addition of 100 ppm citrate to a synthetic waste-cationic ruthenium solution reduced the Kd value for ruthenium on Idaho well sediments to 27 ml/g from 472 ml/g with no citrate. For the same solutions, the reduction on the natural zeolite clinoptilolite was to a Kd value of 4 ml/g from a Kd value of 48 ml/g with no citrate present. Addition of 100 ppm EDTA to the synthetic waste (MTR cooling water) lowered the ruthenium Kd value from about 472 ml/g with no EDTA to 100 ml/g with EDTA. Kepak (1966) reported the adsorption Kd for $Ru(NO)^{+2}$ and Ru^{+3} on hydrated ferric oxide as 8.4×10^3 and 4.8×10^3, respectively.

Jenne and Wahlberg (1968) examined the sediments present in White Oak Creek, Tennessee, identifying their mineralogy and determining a Kd for several elements. The Kd was determined by analyzing the radionuclide content of White Oak Creek water and sediment, and assuming that an equilibrium between the two was attained. The water contained 230 pCi $^{106}Ru/l$, while no measurable ^{106}Ru was found in the sediment. It was concluded that the ^{106}Ru in White Oak Creek water was not being adsorbed by the contacting sediment.

The form of ruthenium in the Clinch River, downstream of White Oak Creek, was suggested by Pickering et al. (1966) to be nitrosyl ruthenium hydroxide. They reported 16 Ci of ^{106}Ru in Clinch River bed sediment as of 1962. Lomenick and Gardiner (1965) reported 1,038 ± 88 Ci of ^{106}Ru concentrated in a small area of White Oak Lake coinciding with two inlet streams that drain the waste seepage pit area. White Oak Lake is above White Oak Creek in the drainage system around Oak Ridge, Tennessee.

Izrael and Rovinskii (1970) studied the groundwater leaching of radionuclides from Russian bomb blast rubble and debris. They used dialysis, electrodialysis extraction and ion exchange to examine the chemical state of several radionuclides. Ruthenium was found to be 19.4% colloidal, 5.1% cationic and 75.5% anionic. The complex makeup of ^{106}Ru showed nearly the same distribution in groundwater solutions of different origin, and had an insignificant adsorptive capacity.

Arnold and Crouse (1971) described problems associated with radioactive contamination of copper recovered from ore fractured with nuclear explosives. The fractured ore was leached with dilute sulfuric acid and the copper was recovered by replacement of scrap iron as copper cement. The ^{106}Ru constituted 42% of the total activity in the leach solution and only the ^{106}Ru was removed along with the copper during the iron replacement reaction.

Amy (1971) studied the adsorption and desorption rates of three ruthenium compounds on acidic and calcareous soils (see Brown, 1976, for a summary of Amy's work). The three compounds were cationic $\mathrm{Ru\ NONO_2\ (NO_3)_2\ (H_2O)_2}$, anionic $\mathrm{Ru\ NO(NO_2)_2\ OH(H_2O)_2}$ and $\mathrm{RuCl_3}$ which produced a preponderance of anionic forms.

R. J. Serne of PNL, 1973, determined ^{106}Ru equilibrium distribution coefficients with the simulated tank waste compositions given in Table 3-9, and seven well sediments described in Table 3-10 under antimony. The ^{106}Ru was added to the simulated tank solutions as $\mathrm{RuCl_3}$ in HCl solution and Kd values obtained as shown in Table 3-69. The form of the ^{106}Ru after addition to the simulated tank solutions is unknown. The traced solution was allowed to remain at 70°C for 48 hours before contact with the sediments.

TABLE 3-69. EQUILIBRIUM DISTRIBUTION COEFFICIENTS BETWEEN SEVEN GLACIOFLUVIATILE SEDIMENTS AND THE SOLUTIONS IN TABLE 3-9 CONTAINING ^{106}Ru. EACH VALUE IS AN AVERAGE OF THREE EQUILIBRATIONS.

	Solution				
Sediments	I	II	III	IV	V
1	2.14	0.13	0.27	0.60	0.34
2	2.01	0.09	0.23	0.53	0.24
3	2.18	0.16	0.18	0.30	0.29
4	2.60	1.79	0.28	0.03	0.53
5	1.04	0.30	0.53	0.58	0.68
6	1.03	0.24	0.40	0.54	0.44
7	1.19	0.41	0	0.15	0.68

Migration Results

Field Studies--

Spitsyn et al. (1958) used an alkaline solution (4 to 8 g NaOH/ℓ, 200 g $NaNO_3$/ℓ) and an acidic solution [6 to 8 g HNO_3/ℓ, 200 g $Al(NO_3)_3$/ℓ] in field studies to determine radionuclide migration rates through soils. Practically no ruthenium was adsorbed from acidic solutions, and no anionic ruthenium was adsorbed by soils. Various radionuclides including ruthenium were injected into the ground in a mixture and migration followed by wells along the migration route. Ruthenium traveled about half as far as strontium.

Haney, Brown and Reisenauer (1962) and Brown and Haney (1964) estimated from the direction and rate of the groundwater flow that 7 to 8 years were required for ^{106}Ru contamination in the groundwater to move from Hanford Purex Plant site to the Columbia River, a distance of nearly 17 miles. The half-life and travel time of ^{106}Ru result in less than 1% of the ^{106}Ru reaching the Columbia River.

Lomenick (1963) discussed ruthenium flow into the drained White Oak Lake bed at Oak Ridge from the intermediate waste pits by surface runoff and groundwater movement. Movement of groundwater in the upper 2 ft of lake bed soil was from 1 to 5 ft/day, while at 2 to 5 ft depth, movement was 0.05 to 0.25 ft/day. The lake bed then (1963) contained about 1200 Ci of ruthenium, with about 70% of the ruthenium in the top 2 ft, or rapid water movement zone, presumably originating at the intermediate level waste pits.

Raymond (1964, 1965) investigated the vertical migration and lateral spread of radionuclides beneath three Hanford waste disposal sites by using scintillation logging of nearby monitoring wells over a period of time.

A disposal site received 7.6 x 10^8 liters of condensate waste containing about 4500 gross beta curies, mostly ^{106}Ru, to 1965. One week after disposal started, contamination was present to 105 ft. Ruthenium had migrated to 130 ft by June 1958, and the entire soil column was contaminated with ruthenium by June 1959. Ruthenium traveled at nearly the same velocity as the soil water.

Brown (1967) gave some profiles of ^{106}Ru at disposal sites. The ^{106}Ru moved at essentially the same velocity as the groundwater, with little or no soil adsorption. Radiochemical analyses of the groundwater yielded a ruthenium pattern of contamination comparable to the size and shape of the tritium and technetium contamination patterns. Limits defined by the 1.0 pCi ^{106}Ru/cm^3 isoconcentration contour in 1966 are given. The disposal site ruthenium concentration was 1000 pCi ^{106}Ru/cm^3 of waste.

Brendakov et al. (1969) added ^{106}Ru to a mountain meadow soil and followed the vertical migration due to precipitation. The average displacement distance from the surface was 3 mm a year after amendment, 7 mm 2 years after amendment and 14 mm 3 years after amendment. The average displacement was defined as: $\overline{X} = \frac{\Sigma pixi}{\Sigma pi}$, where pi = fractional % of the radionuclide in a layer (3 mm thickness) and xi = the depth of the layer in mm. The displacement distance of ^{106}Ru was about the same as the ^{137}Cs and ^{125}Sb also used in the study. These results are not typical for ^{106}Ru migration that ordinarily has been reported to much exceed the migration velocity of ^{137}Cs.

In 1973, the 241-T-106 underground liquid high level waste storage tank at Hanford leaked about 435,000 liters of waste into the surrounding sediments (Anon., 1973). A series of wells were drilled to ascertain the locations and movements of the various radionuclides in the sediment column. Monitoring and core sample analysis showed the relative mobilities of the radionuclides in the high pH, high salt solution. Ruthenium was the most mobile of the radionuclides, having migrated to 27 m (35 m above the water table). The one μCi ^{106}Ru/l soil isopleth was used to delineate the contaminated zone of about 25,000 m^3 of sediments. One of the reactions of the high pH waste with the sediment column involved the chemical attack and partial dissolution of soil minerals (Shade, 1974).

Magno et al. (1970), investigating the radionuclides from the Nuclear Fuel Services plant in Western New York that were migrating through the effluent lagooning system, estimated that 70% of the ^{106}Ru passed through the lagoon system and into nearby surface streams.

Brookins (1976) reported that ruthenium was retained in the shale that surrounded the natural reactor site at Oklo in Gabon. Approximately 1.8 billion years had elapsed since the reactor was active.

Laboratory Studies--

Nishita et al. (1956) leached ruthenium from soils and clay minerals with water and a salt solution. The ^{106}Ru was the most readily leached radionuclide from the soils with water. The ^{106}Ru also was the most easily water-leached from bentonite and kaolinite. The ruthenium tended to be the least exchangeable in both the soils and the bentonite and kaolinite. A persistent fraction of the bentonite and kaolinite adsorbed ruthenium was nonexchangeable.

Essington et al. (1965) used fallout material on soils to determine the leaching effects of water, chelating agents and HCl on ^{106}Ru. Chelating agents (DTPA, CDTA, EDDHA), increased the soluble radionuclides by a small amount as compared to water. The ^{106}Ru tended to remain in the column. Some ^{103}Ru was reported in leachates in CaDPTA-leached soils.

According to Schulz (1965), ruthenium tends to react like manganese, cobalt, zinc, iron and chromium in reactions in a soil environment. They are most soluble in acidic conditions and tend to precipitate as hydroxides as the pH rises. Ruthenium tends to form complexes that are uncharged or negatively charged and would therefore tend to be quite mobile in soils.

Dlouhy (1967) gave ruthenium elution curves from Casaccia soil that were given as the volume of water put through the column versus the fraction eluted at flow velocities of 136 cm/hr and 270 cm/hr. The characteristics of Casaccia soil were not given. The velocity of the ruthenium down the column was obtained in relation to water velocity and a theoretical profile on the soil column derived for field application and estimates. The Kd values for the ruthenium ranged from 1.8 to 2.4 cm^3/g on the soil and 10 to 15 cm^3/g on the tuff. The velocity of the ruthenium divided by the velocity of the water was experimentally determined as 0.11 at the 136 cm/hr water velocity and 0.10 at the 270 cm/hr water velocity.

Eichholz et al. (1967) studied the distribution of ruthenium between suspended sediment particles and aqueous solutions. Natural water samples were characterized and used in the adsorption studies as sources of suspended solids, as shown in Table 3-70. A fission product mixture was added to the natural water samples, the system equilibrated and the water and sediments separated. The adsorption of ^{106}Ru is shown in Table 3-71. A portion of the

^{106}Ru was associated with the suspended sediments, though to a lesser extent than the other radionuclides with the exception of ^{131}I.

TABLE 3-70. PROPERTIES OF NATURAL WATER SAMPLES (EICHHOLZ ET AL., 1967)

Source	Suspended Solids, ppm	Dissolved Solids, ppm	pH	Conductivity μmhos	Solids Composition
Colorado River, Utah	229	300	7.5	540	95% quartz, 5% calcite, feldspar, illite, kaolinite
Camp McCoy, Wisconsin	12	60	6.9	80	30% quartz + feldspar, 6% kaolinite, 24% illite
Bayou Anacoco, Lousiana	24	63	6.2	60	30% quartz, 2% kaolinite, 6% smectite
Lodgepole Creek Nebraska	965	200	6.8	300	20% illite, 80% smectite
Chattahoochee River, Georgia	131	31	7.3	45	33% quartz, 44% kaolinite 23% illite
Billy's Lake Georgia (swamp)	8	68	4.2	45	2% quartz, balance was amorphous and/or organic

TABLE 3-71. ADSORPTION OF ^{106}Ru ON SUSPENDED SOLIDS IN NATURAL WATERS (EICHHOLZ ET AL., 1967)

Source	pH	^{106}Ru Adsorption, %
Colorado River	7.5	25.0
Camp McCoy	6.9	5.7
Bayou Anacoco	6.2	0
Chattahoochee River	7.3	10.4
Billy's Lake	4.2	0

It is obvious that ruthenium adsorption was a function of pH of the water. The higher percentages of adsorbed ruthenium are directly correlated with water pH.

Nishita and Essington (1967) continued work on ^{106}Ru migration in different types of soils, comparing the relative movement of ^{65}Zn, ^{85}Sr, ^{91}Y, ^{106}Ru, ^{137}Cs, ^{144}Ce and ^{147}Pm. Irrespective of the soil type, water leaching resulted in the greatest movement for ^{106}Ru.

Bovard et al. (1968) reported that the free functional groups (carboxylic, phenolic) were the cause of organic matter complexing and fixation of radionuclides. For humic acids, the mean order of complexing was $Ce>Fe>Mn>Co\geq Ru\geq Sr>Cs$. In the case of fulvic acids, no universal order existed. Two types of soils were used in the studies, a calcareous alluvial soil and a humoferruginous podzol. Leaching of fission products, particularly ruthenium, by rainwater occurred essentially in the form of fulvates.

Amy (1971) studied the migration rates of different ruthenium forms in calcareous and acidic soil in columns 30 cm in height by 4.5 cm in diameter. The nitrodinatrato complexes of ruthenium, $RuNONO_2(NO_3)_2\ (H_2O)_2$, were much more mobile than cesium in calcareous soils. About 98 to 100% of the ^{137}Cs remained in the top 4.5 cm of the soil columns, while 38 to 80% of the nitrodinatrato complexes were found in the top 4.5 cm with distribution down the column to 1 to 2% of the ruthenium in the last column section. From 2 to 33% of this ruthenium form passes through the column. For comparison, ruthenium as $RuCl_3$ adsorbs only 10 to 50% in the top 4.5 cm of the soil column, and the dinitro complex, $RuNO(NO_2)_2OH(H_2O)_2$, only 11 to 36%. The fraction from $RuCl_3$ that migrates down the entire column length varied from 3 to 68%, depending on the soil type. In summary, in calcareous soils maximum ruthenium mobility was attained when the ruthenium was in the form of an anionic complex in permeable soils with a sandy texture and low in organic material. Three forms were identified in the column work referred to as A, B, and C. Form A was cationic with a very rapid adsorption rate. Form B was adsorbed very slowly by the soil and was essentially adsorbed to the same degree throughout the column. It may be an anionic form that is evolving toward a cationic form. Form C was present only at the bottom of the soil column if flow rates are very slow. This also was predominately an anionic form also changing toward a more easily adsorbed form. The $RuNONO_2(NO_3)_2(H_2O)_2$ contained Forms A and B in about equal proportions. The $RuCl_3$ contained 15% of Form A, 75% of Form B and 15% of Form C. The $Ru(NO_2)_2(OH)(H_2O)_2$ contained only 5% of Form A and 85% and 10% of

Forms B and C, respectively. Less than 2.5% of any of the above forms passed through the Barthelasse soil which was rich in organic matter. The acidic soils always adsorbed less ruthenium in any form than the calcareous soils. However, like the calcareous soils, the adsorption of ruthenium decreased with the increasing proportion of anionic forms. The calcareous soils, in order to adsorb 50% of the ruthenium, required from 1 to 4 min for the nitrodinatrato complexes, 100 to 300 min for $RuCl_3$ and 200 min to 1 day for the dinitro complexes. The acidic soils, on the other hand, required 7 to 15 min to adsorb 50% of the ruthenium from the nitrodinatrato complexes, 500 min to 1 day from $RuCl_3$ and 1 to 3 days from dinitro complexes. There were indications that the organic matter in acidic soils favored the mobility of all forms of ruthenium.

Champlin and Eichholz (1976) have shown that finely particulate soil materials, such as kaolinite, can adsorb a variety of trace radionuclides including ^{106}Ru and adhere to the soil matrix surface by Van der Waal's forces (Champlin, 1969). Further, these fine particulates were mobilized by laundry detergents and softening agents, so that they were transported quickly through the soil column without reaction with contacting soils.

Summary

Adsorption of Ru^{3+} peaks at pH 6.6 and 14, with a definite correlation between pH and ruthenium Kd for all ruthenium species (Rhodes, 1957; Eichholz et al., 1967; Amy, 1971). Adsorption of all ruthenium species is low at low pH, and little if any adsorption of anionic species occurs at any pH (Spitsyn et al., 1958; Haney et al., 1962; Brown and Haney, 1964; Raymond, 1964, 1965; Brown, 1967; Magno et al., 1970; Schulz, 1965). Some instances of migration on suspended solids have been noted (Champlin and Eichholz, 1976; Eichholz et al., 1967). Hydrated ferric oxide is a good adsorbent for ruthenium (Kepak, 1966). Low ruthenium Kd values have been reported in high salt solutions (Anonymous, 1973; Serne, 1973), probably as a result of nitrate complexing. Migration of most ruthenium complexes through the soil column is relatively rapid (Pickering et al., 1966; Izrael and Rovinskii, 1970; Amy, 1971). Most of the thermodynamic data for the ruthenium complexes do not exist. Thus an estimation of their relative importance in waste disposal operations or spills is difficult, requiring experimental studies for evaluation in each case.

References

Amy, J. P. 1971. Contribution to the Study of the Migration of Ruthenium-106 in Soils. RFP-Trans-140.

Anonymous. 1973. 241-T-106 Tank Leak Investigation. ARH-2874.

Arnold, W. D. and D. J. Crouse. 1971. Radioactive Contamination of Copper Recovered from Ore Fractured with Nuclear Explosions.

Avtokratova, T. D. 1963. Analytical Chemistry of Ruthenium. Israel Program for Scientific Translations.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Bovard, P., A. Grauby and A. Saas. 1968. Chelating Effect of Organic Matter and Its Influence on the Migration of Fission Products. IN: Isotopes and Radiation in Soil Organic Matter Studies. CONF-680275, pp. 471-495.

Brendakov, V. F., A. V. Dibtseva, V. I. Svishcheva, and V. N. Churkin. 1969. Vertical Distribution and Evaluation of the Mobility of Fission Products in Certain Soil Types of the Soviet Union. AEC-tr-7030, pp. 152-170.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Brown, D. J. and W. A. Haney. 1964. Chemical Effluents Technology Waste Disposal Investigations July-December, 1973 - The Movement of Contaminated Ground Water from the 200 Areas to the Columbia River. HW-80909.

Brown, K. W. 1976. Ruthenium: Its Behavior in Plant and Soil Systems. EPA-600/3-76-019.

Champlin, J. B. F. 1969. Transport of Radioisotopes by Fine Particulate Matter in Aquifers. PB-232179.

Champlin, J. B. F. and G. G. Eichholz. 1976. Fixation and Remobilization of Trace Contaminants in Simulated Subsurface Aquifers. Health Physics. 30:215-219.

Cotton, F. A. and G. Wilkinson. 1962. Advanced Inorganic Chemistry. Interscience Publishers.

Dlouhy, Z. 1967. Movement of Radionuclides in the Aerated Zone. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/18, pp. 241-249.

Eichholz, G. G., T. F. Craft, and A. N. Galli. 1967. Trace Element Fractionation by Suspended Matter in Water. Geochim. et Cosmochim. Acta. 31:737-745.

Essington, E. H., H. Nishita and A. J. Steen. 1965. Release and Movement of Radionuclides in Soils Contaminated with Fallout Material from an Underground Thermonuclear Detonation. Health Physics. 11:689-698.

Ginzburg, S. I., N. A. Ezerskaya, I. V. Prokof'eva, N. V. Fedorenko, V. I. Shlenskaya, and N. K. Bel'skii. 1975. Analytical Chemistry of Platinum Metals. Translated by N. Kaner. Israel Program for Scientific Translations.

Goldschmidt, V. M. and C. Peters. 1932. Zur Geochemie der Edelmetalle. Nachr. Adad. Wiss. Gottingen, Math-Physik. Kl.IV:377.

Haney, W. A., D. J. Brown, and A. E. Reisenauer. 1962. Fission Product Tritium in Separations Wastes and in the Ground-Water. HW-74536.

Heath, R. L. 1976. Table of Isotopes. IN: Handbook of Chemistry and Physics. R. C. Weast (ed.), Chemical Rubber Co.

Izrael, Yu. A. and F. Ya. Rovinskii. 1970. Hydrological Uses of Isotopes Produced in Underground Nuclear Explosions for Peaceful Purposes. UCRL-Trans-10458.

Jenne, E. A. and J. S. Wahlberg. 1968. Role of Certain Stream-Sediment Components in Radioion Sorption. U.S.G.S. Professional Paper 433-F.

Kepak, F. 1966. Sorption of the Radioisotopes ^{35}S, ^{131}I and ^{106}Ru on Hydrated Oxides in Laboratory Columns. Collection Czechoslov. Chem. Commun. 31:3500-3511.

Klechkovsky, V. M. 1956. On the Behavior of Radioactive Fission Products in Soil. Their Absorption by Plants and Their Accumulation in Crops. AEC-TR-2867.

Lomenick, T. F. 1963. Movement of Ruthenium in the Bed of White Oak Lake. Health Physics. 9:835-845.

Lomenick, T. F. and D. A. Gardiner. 1965. The Occurrence and Retention of Radionuclides in the Sediments of White Oak Lake. Health Physics. 11:567-577.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Nishita, H. and E. H. Essington. 1967. Effect of Chelating Agents on the Movement of Fission Products in Soils. Soil Science. 102:168-176.

Nishita, H., B. W. Kowalewsky, A. J. Steen, and K. H. Larson. 1956. Fixation and Extractability of Fission Products Contaminating Various Soils and Clays. Soil Science. 81:317-326.

Noddack, I. 1936. Uber die Allgegenwart der Chemischen Elementer. Angew. Chem. 49:835.

Noddack, I. and W. Noddack. 1931. Die Geochemie des Rheniums. Z. Physik. Chem. 54:207.

Pickering, R. J., P. H. Carrigan, T. Tamura, H. H. Abee, J. W. Beverage, and R. W. Andrew. 1966. Radioactivity in Bottom Sediments of the Clinch - Tennessee Rivers. IAEA-SM-72/4.

Raymond, J. R. 1964. Investigation of the Disposition and Migration of Gross Gamma Emitters Beneath Liquid Waste Disposal Sites. HW-81746, pp. 4.32-4.36.

Raymond, J. R. 1965. Cesium and Strontium Distribution Beneath Liquid Waste Disposal Sites. BNWL-235.

Razin, L., V. Khvostov, and V. Novikov. 1965. Platinum Metals in the Essential and Accessory Minerals in Ultramatic Rocks. Geochemistry International. 2:118.

Rhodes, D. W. 1957. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Science Society of America, Proceedings. 21:389-392.

Rhodes, D. W. and J. L. Nelson. 1957. Disposal of Radioactive Liquid Wastes from the Uranium Recovery Plant. HW-54721.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Shade, J. W. 1974. Reaction of Hanford Sediments with Synthetic Waste. ARH-CD-176.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Spitsyn, V. I., V. D. Balukova, A. F. Naumova, V. V. Gromov, F. M. Spiridonov, E. M. Vetrov, and G. I. Gravfov. 1958. A Study of the Migration of Radioelements in Soils. IN: Proc. Second Annual U.N. Conf. Peaceful Uses of Atomic Energy. 18:439-448.

Tischendorf, G. 1959. Zur Genesis einiger Selenidvor Kommen Insbensondere von Tilkerode im Harz. Freiberger Forschungsh. C69:1.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey and R. H. Schumm. 1969. Selected Values of Chemical Thermodynamic Properties. Tables for Elements 35 Through 53 in the Standard Order of Arrangement. Nat. Bur. Stds. Technical Note 270-4.

Wilding, M. W. and D. W. Rhodes. 1963. Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho. IDO-14624.

STRONTIUM

Natural Soil and Rock Distribution

Average strontium contents of igneous and sedimentary rocks are given in Tables 3-72 and 3-73. Note that the strontium contents are often high when compared to the trace concentrations of strontium that may come in contact with them in waste solutions. Vinogradov (1959) reports the average strontium content of soils as 300 ppm. The 300 ppm present as ^{90}Sr in a waste solution would be 42.3 Ci ^{90}Sr/l, for example. Limestone and other calcium-rich sediments and sedimentary rocks tend to be the highest in strontium content due to limited substitution of strontium for calcium in calcite. Strontium carbonate crystallizes in an aragonite type structure when present in sufficiently high concentrations.

TABLE 3-72. AVERAGE STRONTIUM CONTENT OF IGNEOUS ROCKS (TUREKIAN AND WEDEPOHL, 1961) IN ppm

		Granitic		
Ultramafic	Basaltic	High Ca	Low Ca	Syenite
1.0	465	440	100	200

TABLE 3-73. AVERAGE STRONTIUM CONTENT IN SEDIMENTARY ROCKS AND SEDIMENTS (TUREKIAN AND WEDEPOHL, 1961) IN ppm

			Pelagic	
Shale	Sandstone	Limestone	Carbonate	Clay
300	20	610	2000	180

Brief Chemistry

The four naturally-occurring isotopes of strontium include ^{84}Sr (0.55%), ^{86}Sr(9.75%), ^{87}Sr (6.96%) and ^{88}Sr (82.74%). The isotope ^{87}Sr can be locally variable in abundance because it is a daughter of ^{87}Rb. The other isotopes of strontium between ^{80}Sr and ^{95}Sr are radioisotopes. Only ^{90}Sr fission product (half-life 28.1 years), decaying to ^{90}Y, is of sufficiently high yield and long half-life to be of concern in waste disposal operations. The radionuclide ^{89}Sr also is obtained in high yield but the half-life is too short (52 days) to create a persistent disposal problem. The isotope ^{85}Sr (half-life 64 days) is not a fission product, and is usually not encountered except in laboratory waste solutions.

Strontium (II) is the only oxidation state to be encountered in soil-contacted solutions. According to Ahrens (1952) the ionic radius of Sr^{+2} is 1.12 Å, very close to that of Ca^{+2} at 0.99 Å and Ba^{+2} at 1.34 Å. Strontium tends to follow calcium in weathering and other geochemical processes with some exceptions. For example, when present in sufficient concentrations, strontium does form a carbonate that is not isostructural with $CaCO_3$. The other main strontium ore mineral, celestite ($SrSO_4$), is isostructural with its calcium counterpart, anhydrite ($CaSO_4$). However, limestone or calcite ($CaCO_3$) can allow the substitution of several hundred parts per million strontium before there is any tendency for strontianite ($SrCO_3$) to form. As the limestone recrystallizes, there is a tendency for the strontium content to decrease.

There is little, if any, tendency for strontium to form complexes with inorganic ligands. Izrael and Rovinskii (1970), for example, studied by electrodialysis the chemical state of strontium leached by groundwater from rubble produced in a nuclear explosion. They found that 100% of the strontium was Sr^{+2}, with no colloidal or anionic strontium present in the leachate.

Solid Phase and Solution Equilibria

Strontium is an alkaline-earth and forms several salts. Thermodynamic data for various strontium compounds [SrO, $Sr(OH)_2$, SrF_2, $SrCl_2$, $SrCl_2 \cdot 2H_2O$, $\cdot SrCl_2 \cdot 3H_2O$, $SrCl_2 \cdot H_2O$, $SrHPO_4$, $Sr_3(PO_4)_2$, $SrSO_4$, $Sr(NO_3)_2$, $SrCO_3$, $SrSiO_3$, $SrSiO_4$, $SrZrO_3$] were considered in order to determine their stability. Except for $SrSiO_3$, $SrHPO_4$, $Sr_3(PO_4)_2$, $SrCO_3$, and $SrSO_4$, the strontium solid phases are too soluble to show in Figure 3-22. The thermodynamic data for all of these compounds except $Sr_3(PO_4)_2$ were obtained from Parker et al. (1971). The data for $Sr_3(PO_4)_2$ were selected from Sillen and Martell (1964). In an acidic environment, most of the strontium solids will be highly soluble, and if the activity of Sr^{2+} in solution exceeds 10^{-4} moles/liter, $SrSO_4$ can precipitate and would be a stable phase. However, in alkaline conditions, $SrCO_3$ would be the stable phase and the compound that may maintain strontium activity in soil solutions.

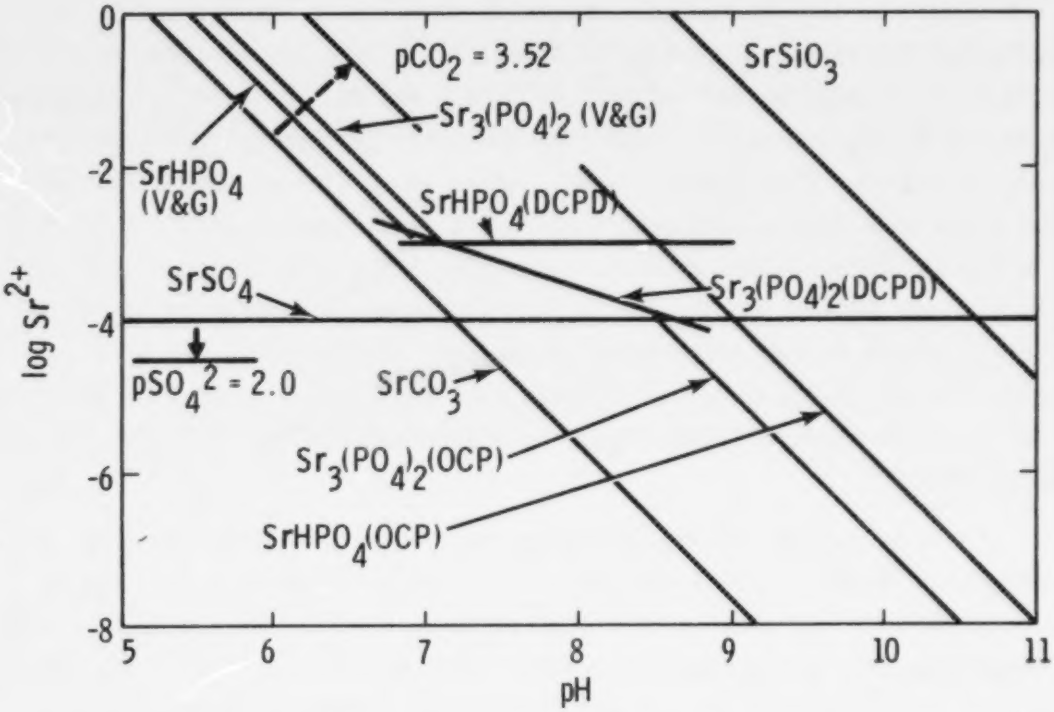

Figure 3-22. The relative stability of various strontium solids at $pCa^{2+} = pSO_4{}^{2-} = 2.5$, $pH_4SiO_4 = 3.1$, and $pCO_{2(g)} = 1.52$ atm in equilibrium with Variscite and Gibbsite (V and G), Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP). Redox potential has little effect on strontium solubilization.

The activity of various solution species in equilibrium with $SrCO_3$ and at anionic activities of $pCl^- = pSO_4{}^{2-} = 2.5$, $pNO_3{}^- = 3.0$, $pF^- = 4.5$, $pH_2PO_4{}^- = 5$ and $pCO_{2(g)} = 1.52$ atm are plotted in Figure 3-23. The thermodynamic data for $SrNO_3{}^+$ and $SrPO_4{}^-$ were obtained from Sillen and Martell (1964). All the other data were obtained from Parker et al. (1971). Although strontium forms complexes with the various anions listed above, the solution complexes do not contribute significantly to the total strontium activity in solution. Sr^{2+} would be the dominant solution species over the environmental pH range of interest and would be expected to be adsorbed by an ion exchange reaction. Izrael et al. (1970) have indicated that strontium was likely to be 100% cationic and that the principal reaction with soils and rocks is ion exchange.

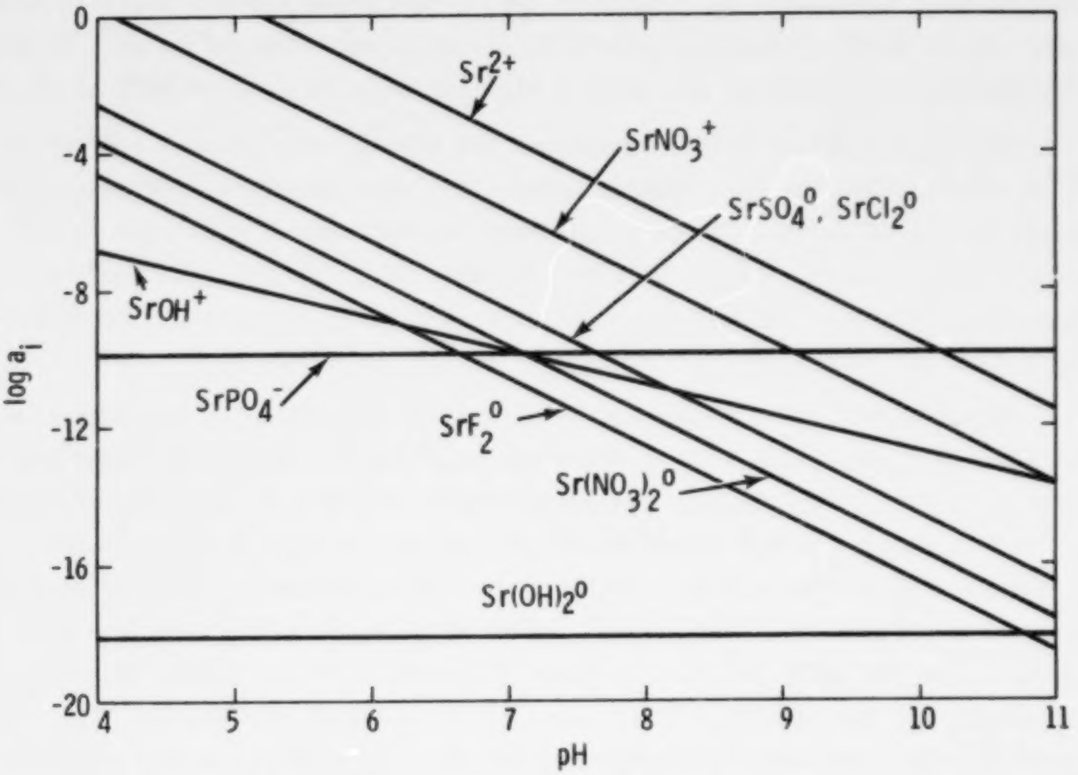

Figure 3-23. The activities of various strontium species in equilibrium with $SrCO_3(s)$ in the soil at $pCl = pSO_4^{2-} = 2.5$, $pNO_3^- = 3.0$, $pF^- = 4.5$, $pCO_{2(g)} = 1.52$ atm and $pH_2PO_4^- = 5.0$.

Experimental Adsorption Results

Amphlett and McDonald (1956) used ^{89}Sr to study cesium and strontium removal by a soil made up of montmorillonite, illite and kaolinite. The equilibrium constant for the reaction $2\ Cs_{soil} + Sr^{+2} \rightarrow 2\ Cs^+ + Sr_{soil}$ was determined as 9.3×10^{-4}.

Rhodes (1957) showed the effect of system pH on the adsorption of strontium from a distilled water solution by a fluviatile Hanford soil. A soil paste pH was 8.6, and the calcite content was 2 wt%. The clay fraction of less than 2 μm was 2 wt% and consisted of primarily montmorillonite, with some mica and chlorite. The system was pH adjusted with NaOH or HCl. The strontium Kd rose from 5 ml/g at pH 6 to 30 ml/g at 8, and 120 ml/g at pH 10. Above pH 10, the sodium added in the NaOH used for pH adjustment began to compete for exchange sites with the strontium, and strontium adsorption began to level off. In 4M $NaNO_3$, strontium adsorption was much less affected by pH. At pH 8, for example, strontium Kd was about 5 ml/g and rose to about 10 ml/g at pH 10.

Rhodes and Nelson (1957) determined the effects of strontium concentration on the strontium distribution between soil and synthetic uranium recovery plant scavenged waste. The soil used here was the same as that used in the above study (Rhodes, 1957). On a log-log plot of strontium concentration in the waste versus strontium concentration on the soil, a straight line relationship resulted indicating ion exchange as a reaction mechanism.

Prout (1958, 1959) showed the effects of pH and strontium concentration on strontium adsorption by Savannah River soil. This soil was 80% sand and 20% clay, chiefly kaolinite. The results were very similar to those of Rhodes (1957) in that a maximum strontium adsorption was reached at about pH 10, although this maximum was much higher (Kd = 700 to 800 ml/g). The effects of competing cations including several sodium nitrate concentrations were also given. The 30% $NaNO_3$ solution is about the same as Rhodes (1957) 4M $NaNO_3$ solution, and the results also are comparable in strontium distribution coefficients. The amount of competing sodium is apparently so high that the soil differences are of lesser importance.

Spitsyn and Gromov (1958) showed that the adsorption of strontium by montmorillonite was an ion exchange process. Various competing cations were added to the strontium-clay system and the strontium distribution coefficient redetermined. These authors also added small amounts of anions such as CO_3^{-2} and $C_2O_4{}^{-2}$ that were said to form radiocolloids with strontium. They believed the enhanced removal of strontium reported by McHenry (1955), when 3×10^{-5} to 3×10^{-4}M PO_4^{-3} was added to wastes contacting calcareous soils, could be attributed to the formation of precipitates as a result of the natural calcium on soil exchange sites reacting with the added phosphate ions. This may be true at some phosphate concentrations, but later study also demonstrated a replacement reaction (Ames, 1959) where calcite reacted with the phosphate to form an apatite.

McHenry (1955, 1958) extensively studied strontium adsorption by a Hanford soil. The Hanford soil had an exchange capacity of 5.90 ± 0.16 meq/100 g, a clay content of 1.15%, a calcite content of 1.50% and a paste pH of 8.4. The soil was calcium-based before use. A comparison of the Hanford composite soil with others is made in Table 3-74 as strontium Kd values from distilled water. The effect of initial strontium concentration on strontium Kd values is also given. The influence of anions on strontium Kd values is shown in Table 3-75. It is probable that replacement of the carbonate in the calcite by oxalate and phosphate ions was underway at the 3×10^{-3}M $C_2O_4^{-2}$ and PO_4^{-3} concentrations, leading to enhanced removal of strontium during the reaction (Ames et al., 1958).

TABLE 3-74. STRONTIUM Kd VALUES FOR WESTERN SOILS
(McHENRY, 1958)

Soil	Kd, ml/g	CEC, meq/100 g	Mechanical Analysis, %			Paste pH
			>50 μm	50-2 μm	<2 μm	
Ringold, E. Wash.	400	34.0	18.6	39.0	42.4	7.2
Warden, E. Wash.	270	6.0	78.1	18.9	3.0	7.3
Bowdoin, E. Mont.	135	13.6	48.5	34.6	16.9	8.3
Hall, C. Nebraska	600	26.3	5.9	60.6	33.5	6.5
Hanford Composite	70	5.8	84.6	11.9	3.5	8.3

TABLE 3-75. THE INFLUENCE OF ANIONS ON THE STRONTIUM Kd IN THE HANFORD COMPOSITE SOIL. ANIONS, AS SODIUM SALTS, WERE PRESENT IN CONCENTRATIONS 10 TIMES AS GREAT AS THE STRONTIUM CATIONS. (McHENRY, 1958)

Sr^{+2}, M	Kd, ml/g				
	NO_3^-	Cl^-	$C_2O_4^{-2}$	SO_4^{-2}	PO_4^{-3}
3×10^{-4}	18.0	25.7	574	24.3	847
3×10^{-5}	49.8	55.9	98.9	61.4	115
3×10^{-6}	65.6	70.3	65.6	72.9	70.3
3×10^{-7}	65.6	72.9	67.9	78.6	75.7

Klechkovsky et al. (1958) determined strontium distribution coefficients on a number of Russian soils, and the effects on strontium Kd of competing Ca^{+2} and K^+. The competing cations lowered the strontium Kd in proportion to their concentrations.

Sorathesn et al. (1960) obtained some strontium distribution coefficients on Clinch River sediments that were in the ten thousands, much higher than for standard clays equilibrated with the same solution. The difference was thought to be due to the organic material in the river sediment. Benson (1960) reviewed the strontium work with soils at Hanford up to 1960.

Baker and Beetem (1961) studied the distribution coefficients for carrier-free strontium on an Alaskan wind-blown silt with various concentrations of competing cations which were to be expected at the site. One or two of the Kd values exceed the experimental limits by large amounts, but the remaining values conform to a straight line plot of strontium Kd versus the inverse sum of the competing calcium and magnesium concentrations as required by ion exchange theory (Kaufman, 1963).

Cohen and Gailledreau (1961) investigated strontium adsorption on Saclay soil consisting of 45% montmorillonite, 45% kaolinite and 10% illite. The cation exchange capacity was 210 meg/100 g. Graphs were presented of trace strontium-macrocalcium, trace strontium-macrosodium and trace strontium-macropotassium systems. Some work was performed on three-component ion exchange systems. It was shown that the Kd values plotted versus the strontium concentration for the above Saclay soil yielded a straight line on log-log scales as required by ion exchange theory.

Goldberg et al. (1962) measured the strontium distribution between ground Rainier Tuff and a synthetic groundwater solution at 1-day and 7-days equilibration times. There was marked time dependency on strontium adsorption by the 100 to 200 mesh tuff. Comparable solutions yielded a 7-day strontium Kd of 3000 ml/g and a 1-day strontium Kd of 500 ml/g.

Angelo et al. (1962) measured strontium Kd values on 32 to 80 mesh basalt and obtained values ranging from 16 ml/g to 135 ml/g, depending on the amount of salt in the contacting solution. The lesser values correlated with the higher salt contents.

Janzer et al. (1962) examined strontium adsorption on Project Gnome rock samples. The strontium Kd ranges obtained are listed in Table 3-76. The rock types are described in Table 3-24. One sample part was equilibrated with non-traced solution, with the tracer added later. The five equilibrating solutions varied from 1,000 to 45,000 mg/l in dissolved solids and each experiment was run in triplicate. The strontium Kd values are given as minimums for the highest dissolved solids to maximums for the lowest dissolved solids. A membrane technique was used to separate solids and solution.

TABLE 3-76. SUMMARY OF STRONTIUM Kd VALUES (JANZER ET AL., 1962)

Sample	Kd, ml/g Minimum	Kd, ml/g Maximum
45	8	20
95	8	23
320	10	29
331	3	22
350	8	16
365	9	16
380	6	12
479	8	17
510	5	14
526	8	17
552	7	15
620	6	14
653	0.6	9
680	0.7	11

Baetsle et al. (1962, 1963) gave the range in strontium Kd values with soils at Mol, Belgium, that consisted chiefly of quartz sand as 1.7 to 38 ml/g at pH 7.7 with tap water. Dynamic or column Kd values were compared to static determinations. Problems were encountered in obtaining adequate Kd values derived from column breakthrough data because physical flow phenomena were superimposed on the effects due to radionuclide adsorption reactions. Batch adsorption data were easier to obtain and free of problems associated with column physical flow phenomena.

Beetem et al. (1962) determined strontium Kd values on granodiorite from the Climax stock with synthetic groundwater. The 100 to 200 mesh samples were equilibrated for 72 hr and yielded strontium Kd values of 4 to 9 ml/g. The 0.5 to 1.0 mm granodiorite was equilibrated for 720 hr and yielded Kd values of from 11 to 23 ml/g, probably due to the longer contact time.

Kokotov et al. (1961, 1962) gave Kd values for strontium on six Russian soil types as a function of pH. The replacement series Sr > Ca > Mg > K $\geq$ NH_4 > Na was given for strontium competing cation efficiency.

Stead (1963) referred to strontium Kd values of 5 to 14 ml/g on a dolomite from the Rustler formation when the groundwater had 4250 mg/l of total dissolved solids. The average Kd was 10 ml/g.

Berak (1963) used the same solution and conditions shown in Table 3-20 under cesium to determine strontium Kd values of a number of rocks and minerals. The diameter of the solid particles was 0.1 to 0.2 mm. The concentration of carrier strontium was 1×10^{-5}M as $SrCl_2$. The strontium distribution coefficients are given in Table 3-77. Strontium discrimination factors were determined on several rocks and minerals by using a solution containing 10^{-5}M Sr $(NO_3)_2$ + ^{90}Sr and 2.5×10^{-3}M Ca^{+2}. After equilibration, ^{90}Sr was determined by radioassay and Ca^{+2} by complexometric titration. The fraction of ^{90}Sr on the solid divided by the fraction of Ca^{+2} retained on the solid constitutes the strontium discrimination factor at the strontium and calcium concentrations and ratios used. The results are listed in Table 3-78.

TABLE 3-77. STRONTIUM DISTRIBUTION COEFFICIENTS FOR SEVERAL ROCK, MINERAL AND SOIL TYPES

Rock	Sr Kd, mg/l	Condition	Reference
Alluvium, Central Nevada	48-2454	500-4000 μm	Nork et al., 1971
Silty Clay, Idaho	240	Quartz, illite, apatite	Wilding and Rhodes, 1963
Silty Clay, Idaho	220	Quartz, illite, apatite	Wilding and Rhodes, 1963
Clinch River, Tenn. bottom sediments	545 - 1 hr 1690 - 3 days 1438 - 7 days	pH 6	Carrigan et al., 1967
	659 - 1 hr 3537 - 3 days 4024 - 7 days	pH 9	

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
Sandstone, fine, light gray	1.26 1.13 1.88	4000 μm 500 μm <62 μm	Sokol, 1970
Shaley siltstone, carbonaceous, black	8.32 9.41 9.56	4000 μm 500 μm <62 μm	Sokol, 1970
Sandstone, fine, light gray	1.37 1.36 2.08	4000 μm 500 μm <62 μm	Sokol, 1970
Sandstone, very fine, silty, dark gray	7.76 8.37 9.79	4000 μm 500 μm <62 μm	Sokol, 1970
Shaley limestone, New Mexico	8.32	>4000 μm	Nork and Fenske, 1970
Sandstone, New Mexico	1.37	>4000 μm	Nork and Fenske, 1970
Alluvium, INEL, Idaho	7.2-10.5 40	(Laboratory) (Field)	Schmalz, 1972
Tuff, Rainier Mesa, Nevada	260	>400 μm	Nork and Fenske, 1970
Tuff, Rainier Mesa, Nevada	2070-3480	100-200 mesh	Goldberg et al., 1962
Tuff, Rainier Mesa, Nevada	1700-4300	---	Kaufman, 1963
Tuff, NTS, Nevada	4000	---	Stead, 1964
Limestone, Yucca Flat, Nevada	0.19	>4000 μm	Nork and Fenske, 1970
Granodiorite, Climax stock	4-9 11-23	100-200 mesh 0.5-1 mm	Beetem et al., 1962
Granite, Central Nevada	1.7	>4000 μm	Nork and Fenske, 1970
Basalt, Buckboard Mesa, Nevada	16-135	32-80 mesh	Angelo et al., 1962
Basalt, Amchitka	220	500-4000 μm	Essington and Nork, 1969
Basalt, Amchitka	1220 1.1 (seawater)	500-4000 μm 500-4000 μm	Essington and Nork, 1969

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
SUPERSATURATED ROCKS (contain quartz)			
Rhyolites, Czechoslovakia	56	0.1-0.2 mm	Berak, 1963
	15		
	7		
	6		
	33		
	30		
	25		
	41		
	12		
	4		
	12		
	9		
	9		
	21		
	12		
	31		
	37		
	0		
Volcanic Glasses, East Slovakia	7	0.1-0.2 mm	Berak, 1963
	32		
	1		
	11		
Central Slovakia	13		
Iceland	3		
	6		
Rhyodacites, East Slovakia	11		
Dacites, Slovakia	16	0.1-0.2 mm	Berak, 1963
	43		
	21		
	27		
Quartz Porphyries, Central Bohemia	18	0.1-0.2 mm	Berak, 1963
Bohemia	8		
	47		
	6		
North Bohemia	8		
SATURATED ROCKS (contain no quartz or feldspathoids)			
Trachytes, North Bohemia	39	0.1-0.2 mm	Berak, 1963
Slovakia	12		
Andesites, Central Slovakia	11	0.1-0.2 mm	Berak, 1963
	13		

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
Pyroxenic, East Slovakia	17		
	13		
	37		
	16		
	30		
Garnetic, East Slovakia	32		
Altered,	21		
Pyroxenic,	48		
Propylletized	20		
Granul. pyrox., vitreous	50		
Spillites, albitized		0.1-0.2 mm	Berak, 1963
Proterozoic basalt, Central Bohemia	8		
Diabases, Bohemia	0	0.1-0.2 mm	Berak, 1963
	1		
	10		
	25		
	32		
	30		
	39		
	45		
North Moravia	1		
Melaphyres, basalt		0.1-0.2 mm	Berak, 1963
North Bohemia	212		
	35		
	5		
Slovakia	10		
Basalts, North Bohemia	187	0.1-0.2 mm	Berak, 1963
Vitreous	6		
	22		
	80		
	33		
	32		
UNDERSATURATED ROCKS (Nonfeldspathoidal)			
Picrites, North Moravia	64	0.1-0.2 mm	Berak, 1963
	64		
	43		
	85		
	85		
	64		
	51		
	108		
	9		

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
Teschenites with olivine,		0.1-0.2 mm	Berak, 1963
North Moravia	74		
	30		
	22		
	38		
	25		
	46		
Picrites, North Moravia	92	0.1-0.2 mm	Berak, 1963
	13		
Peridotite, North Moravia	35		
Pyroxenite, NW Bohemia	0		
	0		
Monchiquite with olivine,	35	0.1-0.2 mm	Berak, 1963
North Moravia			
Ouachitite, with apatite	7		
North Moravia	52		
Olivine basalts, N. Bohemia	321		
East Slovakia	322		
Central Slovakia	324		
North Bohemia	334		
UNDERSATURATED ROCKS (with feldspathoids)			
Phonolites, North Bohemia	15	0.1-0.2 mm	Berak, 1963
	7		
	140		
	75		
Tephrites, North Bohemia,			
chabazite	86	0.1-0.2 mm	Berak, 1963
leucite	26		
chabazite	44		
nepheline	143		
nepheline-leucite	83		
leucite	65		
leucite	80		
Basanites, North Bohemia,			
nepheline-leucite	32	0.1-0.2 mm	Berak, 1963
	0		
	22		
	38		
	59		
	0		
Nephelinites, Melilite,			
NW Bohemia	5	0.1-0.2 mm	Berak, 1963
leucite	22		
olivine-nepheline basalt	28		
	60		

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
Leucitites, NW Bohemia	56	0.1-0.2 mm	Berak, 1963
	82		
	33		
nepheline	16		
Melitites, olivine-hauyne basalt	29	0.1-0.2 mm	Berak, 1963
MINERALS			
Quartz	5	0.1-0.2 mm	Berak, 1963
Agate	9		
Chalcedony	0		
Opal	0		
Olivine	3		
Chondrodite	10		
Thaumasite	0		
Leucophanite	18		
Zircon	35		
Topaz	8		
Kyanite	0		
Sillimanite	9		
Staurolite	8		
Garnet, almandine	0		
Garnet, grossular	0		
Garnet, andiadite	0		
Garnet, uvarovite	2		
Hydrogarnet	24		
Vesuvianite	0		
Sphene	0		
Rinkite	10		
Axinite	0		
Hemimorphite	14		
Beryl	0		
Dioptase	15		
Tourmaline	0		
Wollastonite	8		
Rhodonite	5		
Hypersthene	4		
Aegirine	14		
Augite	2		
Diopside	3		
Enstatite	3		
Jeffersonite	16		
Tremolite	6		
Chrysotile	2	0.1-0.2 mm	Berak, 1963
Sepiolite	30		
Attapulgite	5		
Palygorskite	8		
Zoisite	0		

TABLE 3-77. (continued)

Rock	Sr Kd, mg/l	Condition	Reference
Talc	0		
Pyrophyllite	0		
Biotite	5		
Muscovite	5		
Chlorite Penninite	2		
Chlorite, Dellesite	0		
Sericite	2		
Illite	100		
Glauconite	25		
Celadonite	35		
Serpentine	0		
Kaolinite	15		
Halloysite	58		
Allophane	71		
Hisingerite	97		
Smectites	104		
	150		
	96		
	138		
	150		
	217		
	163		
Nontronite	187		
Apophyllite	10		
Melilite	5		
Feldspars, Orthoclase	10		
Sanidine	23,11		
Albite	10		
Oligoclase	11		
Andesine	10		
Laboradorite	8		
Scapolite	11		
Leucite	11		
Analcite	25		
Pollucite	7		
Nepheline	0		
Sodalite	3		
Cancrinite	14		
Zeolites:			
Mordenite	27	0.1-0.2 mm	Berak, 1963
Stilbite	166		
	25		
Heulandite	47		
Faujasite	34		
Harmotone	12		
Chabazite	210		
Natrolite	8		
Scolecite	4		

TABLE 3-78. MICROSTRONTIUM-MACROCALCIUM DISCRIMINATION ON SOME 0.1 to 0.2 mm ROCKS AND MINERALS (BERAK, 1963)

Mineral	Strontium Discrimination Coefficient
Halloysite	1
Montmorillonite	1
Sepiolite	2.3
Chlorite	1
Dellesite	9
Soclalite	>9
Analcite	2
Cancrinite	12
Leucite	3
Orthoclase	9
Orthoclase	11
Microcline	8
Albite	9
Labradorite	9
Mordenite with quartz	1.6
Heulandite	48
Heulandite	55
Heulandite	19
Mordenite	1.3
Faujasite	4
Harmotome	>9
Brewsterite	>24
Phillipsite	8
Chabazite	14
Natrolite	9
Scolecite	>9
Thomsonite	>34
Thomsonite	10.2
SILICATE ROCKS	
Basalt	17
Nepheline tephirite	2
Nephelinite	10
Nepheline-leucite tephirite	4
Olivine hauyne nephelinite	5
Leucite tephrite	5
Leucite tephrite	4
Leucitite with phillipsite	8
Tephrite with chabazite	5

Basalt mineralogy - augite, 40%
plagioclases, 50%
magnetite, 8%
apatite, 1%

Nephelinite - Ti-augite, 68%
magnetite, 12%
nepheline, 10%
plagioclase, 7%
leucite, 3%

The data of Table 3-77 show that the secondary silicates, such as the clay minerals and certain zeolites, give much higher Kd values for strontium than the primary igneous minerals found in rocks, such as quartz and feldspars Some of the secondary silicates can also discriminate between geochemically similar calcium and strontium, as seen in Table 3-78.

Tamura and Struxness (1963) outlined several strontium removal mechanisms that could apply to soil solutions. Two ion exchange reaction types were postulated. One type involves simple ion exchange on a relatively pH-stable substrate such as zeolite. The other type was exemplified by alumina that is amphoteric as a substrate for ion exchange. The differences were further elucidated by Tamura (1964). Strontium Kd values as high as 30,000 were measured in alkaline systems on alumina. The strong influence of soil sesquioxides in strontium removal was emphasized.

Baetsle et al. (1964) have given data (Table 3-79) on Kd values for strontium with Belgian soils. The strontium exchange work on Mol, Belgium, soils was with deionized water, mains water (tap water?) and groundwater. None of the water compositions were given. The pH was given probably as measured in the eluting solution prior to the equilibrations. The Kd values were obtained by adsorbing a band of ^{89}Sr on the top of a soil column and eluting with the solution indicated. Samples of the effluent were counted and the Kd determined from the $C/C_o = 0.5$ as indicated above. The results were part of a study to compare static and dynamic Kd values.

TABLE 3-79. VARIATION OF TRACE STRONTIUM Kd VALUES WITH pH (BAETSLE ET AL., 1964)

	Kd, ml/g					
	Deionized	Mains Water		Groundwater		
Soil Type	Water, pH4	pH 7.7	pH 3	pH 4	pH 5	pH 7
Eolian Sand						
Horizon A	16-22	38	7	2.0-2.8	3.6-5.8	5-7
Horizon B	1.5- 1.6	10	13	--	--	--
Horizon C	0.5- 0.9	3.5	12	--	--	--
Mol White Sand	0.95	1.7	4.5	2.1-2.5	5.4-5.6	4.7-4.9
Mol Lignitic Sand	--	--	--	2.0-3.1	5.0-5.5	6.8-7.4

The mains water Kd values are higher due to the higher pH. However, the higher mains water Kd values at pH 3 were difficult to rationalize. They should be lower than both the deionized water Kd values and the mains water Kd values at pH 7.7.

A Burns, Mississippi, montmorillonite, with the composition shown in Table 3-80, was used in macroion systems of potassium, calcium and magnesium to obtain Kd values and calculated Kd values in mixed two and three ion systems (Baetsle et al., 1964). The selectivity coefficients given were $K_{Sr}^{K} = 0.096$ ($Sr_{mont.} + 2K^{+} \rightarrow 2K_{mont.} + Sr^{+2}$), $K_{Sr}^{Mg} = 1.08$ ($Sr_{mont.} + Mg^{+2} \rightarrow Mg_{mont.} + Sr^{+2}$) and $K_{Sr}^{Ca} = 0.98$ ($Sr_{mont.} + Ca^{+2} \rightarrow Ca_{mont.} + Sr^{+2}$). The isotherm of the binary systems were obtained at several ionic strengths such as 0.1N, 0.01N and 0.001N. Kd values for strontium, for example, in a Ca-Mg system were then obtained by plotting the log of magnesium, calcium or some other macroion concentration versus the Kd to allow extrapolation of the resulting straight line relationship. Thus, the various binary system selectivity coefficients and Kd values determined for each macroion are used to determine a Kd in the binary macroion system. Mercer (1966, 1967) has conducted similar studies on zeolite ion exchange from multicomponent systems and gave a table comparing his predicted strontium Kd results with those of Baetsle et al. (1964) on the Burns, Mississippi montmorillonite (Table 3-81). Clinoptilolite gave an experimental strontium Kd value of 733 ml/g from a macroion system 0.0104 meq NH_4^{+}/ml + 0.0891 meq Na^{+}/ml, and a strontium Kd value of 160 from a macrosystem of 0.0170 meq Na^{+}/ml + 0.0830 meq Ca^{+2}/ml.

Wahlberg et al. (1965) studied the ion exchange adsorption of strontium from calcium, magnesium, sodium and potassium solutions by kaolinite, montmorillonite and illite. The adsorption of strontium was described by the mass-action equilibrium equation. Calcium provided the greatest competition for strontium, and sodium the least. The data are presented in graphic form as Sr^{+2} normality (from 10^{-10}N to 10^{-1}N) versus strontium distribution coefficient (Kd). The clays used were American Petroleum Institute standards, well-characterized in the clay literature.

TABLE 3-80. COMPOSITION OF BURNS, MISSISSIPPI, MONTMORILLONITE. CAPACITY WAS 1.04 meq/g (BAETSLE ET AL., 1964).

Constituent	Wt %
S_1O_2	51.29
Al_2O_3	15.96
Fe_2O_3	2.46
FeO	0.14
TiO_2	0.18
CaO	2.21
MgO	3.95
Na_2O	0.05
K_2O	0.13
H_2O^-	18.00
H_2O^+	5.37
Total	99.74

TABLE 3-81. COMPARISON OF EXPERIMENTAL AND COMPUTED STRONTIUM Kd VALUES FOR BURNS MONTMORILLONITE (MERCER, 1967)

Concentration, meq/ml			Experimental	Baetsle	Mercer
C_K	C_{Mg}	C_{Ca}	Kd, ml/g	Kd, ml/g	Kd, ml/g
0.0855	0.01382	--	24.8	21	10
0.0404	0.00962	--	59.5	41	33
0.0143	0.00604	--	135.5	102	102
0.00702	0.00412	--	207.0	177	191
0.00240	0.00282	--	369.7	368	352
--	0.0180	0.0769	12.17	12.1	11
--	0.0146	0.0348	20.6	21.3	21
--	0.0106	0.0096	56.9	53.2	53
--	0.0068	0.0032	114.3	106.8	109
--	0.0043	0.0009	193.5	221.8	212
0.0885	--	0.0124	18.0	22.0	10
0.0411	--	0.00850	50.0	48.0	33
0.0155	--	0.00520	116.0	111.0	102
0.00612	--	0.00360	193.0	203.0	206
0.00582	--	0.00248	336.0	300.0	285
--	0.0852	0.0128	12.3	14.5	11
--	0.0388	0.0114	25.8	24.5	22
--	0.0100	0.0074	58.6	55.0	62
--	0.0046	0.0056	100.6	107.0	104
--	0.0015	0.0036	244.1	209.0	206

Hawkins and Short (1965) completed an experimental design to allow multiple regression analysis of the effects on strontium and cesium Kd values of the following ions and their concentration ranges: Ca^{+2}, 5-500 ppm; Na^{+}, 6-650 ppm; K^{+}, 1-100 ppm; NH_4^{+}, 1-100 ppm; Mg^{+2}, 1-125 ppm; Cs^{+}, 0.05-5 ppm; PO_4^{-3}, 0.1-10 ppm; and pH 4-9. The equation for strontium adsorption may be applicable to other soils besides INEL, Idaho soils, if they do not contain abundant sesquioxides.

Wahlberg and Dewar (1965) studied ion exchange adsorption of trace concentration strontium ($10^{-10}N$ ^{85}Sr) as affected by two competing cations. The Kd values calculated with the mass-action equation agreed most closely with high exchange montmorillonite than with lower capacity kaolinite.

Dlouhy (1967) investigated strontium and other cations adsorbed by Cascaccia soil and tuff as a function of pH, time and solution composition. Kd values were used in chromatographic equations to show the radionuclide distribution beneath disposal sites. Strontium Kd values ranged from 6 to 15 ml/g in the soil to 45 to 75 ml/g in the tuff.

Hajek and Ames (1968) compared batch and small column Kd values for strontium and cesium on a Burbank loamy fine sand containing up to 2 wt% calcite. The soil to solution ratio was varied between 100 to 5 for the batch Kd determinations. Strontium Kd values tended to decline as the solution to soil ratio declined. The small columns did not yield a real Kd value for strontium unless it was preleached with at least 450 column volumes of 3N $NaNO_3$. It is probable that calcium from the calcite was solubilizing and competing with the strontium during the batch tests. Pre-equilibration of the soil with the solution to be used minus the strontium radioisotope is a must before Kd values are measured. Gardner and Skulberg (1964) had similar Kd changes with solid-solution ratio changes.

Jenne and Wahlberg (1968) found that the adsorption of ^{90}Sr was controlled by in situ precipitation of calcium carbonate in a small stilling basin sample in White Oak Creek, Tennessee. The clay minerals controlled only the adsorption of cesium while manganese and iron oxides controlled ^{60}Co removal.

Cerrai et al. (1969) reported that the strontium Kd on a marine sediment from a core at 50 m off La Spezia, Italy, was 6.3 ml/g.

R. J. Serne (PNL), 1973, determined strontium distribution coefficients from high salt, high pH, synthetic tank solutions with Hanford core well sediments. The chemical composition of the synthetic tank solutions are given in Table 3-9 and the sediment characteristics in Table 3-10 under antimony. The strontium Kd values in Table 3-82 are the average of three values. The relatively low strontium Kd values obtained were principally due to the high concentrations of competing cations present.

TABLE 3-82. STRONTIUM Kd VALUES (ml/g)

Sediment	Solution				
	I	II	III	IV	V
1	3.91	1.74	0.023	0.0	18.40
2	2.90	1.17	0.047	0.0	8.40
3	2.93	1.22	0.072	0.0	12.87
4	12.40	5.44	0.074	0.0	173.84
5	1.87	0.81	0.13	0.17	12.70
6	2.50	0.95	0.10	0.14	39.20
7	1.86	0.87	0.08	0.23	20.16

Routson (1973) determined strontium adsorption characteristics of three Hanford project soils. The soils were well-characterized as shown in Table 3-83. The clay fractions (0.2 to 2 μm and <0.2 μm) were analyzed by X-ray diffraction and found to be very similar for the three soils. The Ritzville silt loam, Burbank loamy sand and Ephrata sandy loam showed montmorillonite as the dominant mineral in the 0.2 to 2 μm fraction, with lesser amounts of vermiculite and mica. Montmorillonite was the only clay mineral detected in any of the <0.2 μm fractions. There was no evidence of clay mineral weathering after deposition of the parent materials. The only indication of soil weathering is the accumulation of calcium carbonate in the upper C horizons of all three soils. The strontium Kd values are given in Table 3-84. The original soil samples had chiefly calcium in the exchange positions. Note that the sodium based soils showed higher strontium Kd values, indicating that calcium displaced strontium when present in the system. It can also be seen in Table 3-84 that calcite removal from the soils was the most effective way to raise the strontium Kd values.

TABLE 3-83. CHARACTERISTICS OF THE SOILS USED IN STRONTIUM Kd DETERMINATIONS (ROUTSON, 1973)

		Particle Size % of Soil Fraction			$CaCO_3$ % of Total	Fe_2O_3 % of Total	Organic Carbon % of Total
		Sand	Silt	Clay			
Ritzville							
A_{11}	0-2 in.	23.3	64.1	12.6	--	1.50	--
A_{12}	2-18 in.	47.0	46.0	7.0	0.8	1.44	0.34
B_1	18-27 in.	54.7	42.5	2.5	1.3	0.89	0.27
C_{ca}	27-41 in.	39.8	57.7	3.3	8.9	1.09	0.13
C	41-72 in.	55.0	42.0	3.0	4.2	1.11	0.17
Burbank							
A_{11}	0-3 in.	76.8	16.8	6.4	--	0.80	--
A_{12}	3-16 in.	91.2	7.6	1.2	0.7	0.84	0.16
AC	16-22 in.	88.7	10.6	0.7	1.6	0.62	0.14
AC_2	22-30 in.	82.5	16.4	1.1	5.5	0.52	0.13
IC	30 in. +	79.8	16.2	4.0	3.5	0.39	0.20
Ephrata							
A_{11}	0-3 in.	44.2	47.1	8.7	--	1.22	--
A_{12}	3-12 in.	59.0	36.9	4.1	0.57	1.25	0.18
B_1	12-15 in.	57.4	39.3	4.3	0.70	1.20	0.13
IB_2	15-19 in.	62.9	31.4	5.7	0.87	0.98	0.29
IIC	19-24 in.	92.1	5.4	2.5	3.28	0.46	0.26

TABLE 3-84. TRACE STRONTIUM ADSORPTION CHARACTERISTICS FROM 0.2N NaCl (ROUTSON, 1973)

	Equilibrium Distribution Coefficients (ml/g)				
	No Pretreatment	Na-Based	Organic Carbon Removed	Calcite Removed	Organic C and Calcite Removed
Ritzville					
A_{12}	21	109	37	189	96
B_1	27	131	46	257	101
C_{ca}	27	84	40	71	61
C	24	58	43	82	66
Burbank					
A_{12}	12	57	20	106	45
AC	15	41	28	91	61
AC_2	21	53	35	67	65
IC	17	48	38	81	52
Ephrata					
A_{12}	12	73	21	115	44
B_1	12	68	22	126	57
IB_2	17	82	33	166	96
IIC	23	55	55	145	70

Jackson (1976) used tracers to study adsorption of seven radionuclides, including strontium, on copper ore and decomposition products during copper leaching, as a function of ore particle size, solution composition, pH and liquid/solid ratio. The reactions were carried out in autoclaves for up to 8 months in a controlled oxygen pressure and 363 K. The solids continued to concentrate strontium from the liquid for a long period of time as the ore and gangue surfaces continued to change and grow other mineral phases. A substantial amount of activity was adsorbed by the ore and gangue decomposition products (gypsum, jarosite, anhydrite). As an example, in one long-term experiment, the strontium Kd was 0.25 ml/g at time zero and 499.6 ml/g at zero plus 173.6 days.

Migration Results

Field Studies --

Mawson (1956) and Evans (1958) reported the results of studies on fission product radionuclide movements after disposal in sand at Chalk River, Ontario. In dilute, neutral pH wastes ruthenium moved much more rapidly through the sand than did strontium. When acid wastes were disposed into the same sand, strontium and ruthenium both moved rapidly and at about the same speed through the sand.

Spitsyn et al. (1958) used an alkaline solution (4 to 8 g NaOH/l, 200 g $NaNO_3$/l) and an acidic solution (6 to 8 g HNO_3/l, 200 g $Al(NO_3)_3$/l) in field studies of radionuclide migration. A mixture of radionuclides were injected into the sandy soil and the movement traced by wells along the migration route. Strontium traveled the farthest, with ruthenium traveling about half as far as strontium. The authors concluded that the groundwater into which the strontium is disposed should have a low calcium and general dissolved solids content.

Parsons (1961) described the movement of fission products from a surface disposal site in Chalk River, Ontario, through the near-surface groundwater, resulting from a 1954 experimental disposal of 5700 liters of waste containing 2100 kg of ammonium nitrate. The high concentration of ammonium ions caused all of the strontium to move off relatively rapidly with the groundwater. Horizontal movement of the waste was rapid enough to reduce vertical dispersion, and the strontium remained close to the top of the water table and traveling at 0.027 times the velocity of the groundwater.

Parsons (1963) described a 1954 disposal of 3800 liters of acid waste containing complexing agents and over 1000 Ci of ^{90}Sr. The waste was poured into a pit lined with limestone. Sampling of the sandy soil and near-surface groundwater allowed the movement of fission products to be followed. The ruthenium migrated rapidly, traveling at nearly the same velocity as the groundwater. The ^{90}Sr became separated from the ruthenium, developing into a continuous tongue 198 m long, 3 to 4 m thick and containing 800 Ci of ^{90}Sr. The ruthenium entered a shallow lake in 1957, while the ^{90}Sr remained more deeply buried and traveling much more slowly.

The migration of ^{90}Sr as seepage from Oak Ridge burial pits was investigated by Lomenick et al. (1967). They reported that most of the strontium on the side walls and bottom of the pit in Conasauga shale was tied up in the precipitated calcite (calcium carbonate). Water moved 0.15 m/day while the ^{90}Sr moved 0.24 m/yr.

Mortensen and Marcusiu (1963) incubated a silty clay loam with 40 μCi ^{90}Sr for 60 days and obtained hot water extractions or hydrolyzed with 6N HCl. The supernatant liquid was electrodialyzed with ^{90}Sr migrating to the anode compartment suggesting negatively charged ^{90}Sr-organic matter complexes. Gel filtration showed that ^{90}Sr was complexed or held on exchange sites by high molecular weight polymers. The radioactivity correlated with the presence of polyuronides. Phenols, amino acids and keto acids were separated from the 6N HCl hydrolysate by paper electrophoresis, with no clear correlation between radioactivity and these components.

Brown (1967) reviewed the hydrology and geology of two contaminated waste disposal trenches at Hanford. Several wells were drilled in and around the disposal sites and the ^{90}Sr and moisture determined in the sediment column beneath the disposal sites. The bulk of the ^{90}Sr activity was contained in a 15 meter vertical section immediately below the bottom of the disposal sites. The average strontium concentration was 10^{-1} μCi ^{90}Sr/g sediment in the 15 meter high strontium concentration zone and fell off rapidly below this zone to 10^{-4} μCi ^{90}Sr/g sediment. Spatially anomalous ^{90}Sr distributions were correlated with changes in lithology. Contaminated sediment columns containing 0.15 μCi ^{90}Sr/g were used to determine the effects of groundwater leaching on ^{90}Sr movement. Fifty column volumes of groundwater removed 4% of the ^{90}Sr from the sediment column and 500 column volumes removed 31% of the ^{90}Sr adsorbed on the sediments.

Magno et al. (1970) investigated the migration of strontium through the effluent lagooning system of the Nuclear Fuel Services plant in western New York State. They estimated on the basis of analyses that approximately 90% of the ^{90}Sr passed through the lagoon system and into nearby surface streams. Further, only 12% of the ^{90}Sr discharged from the lagoon system was associated with suspended solids. Thus 78% of the ^{90}Sr discharged from the lagoon system was in solution. The low adsorption of ^{90}Sr was apparently due to a combination of pH and competing cations lowering ion exchange loading of solids. For example, when the plant effluent pH was 11 during one sampling period, 75% of the ^{90}Sr was removed in the lagoon system. At another sampling period, plant effluent was pH 7 and only 10% of the ^{90}Sr was removed by the lagoon system.

Merritt (1967, 1976) reported on the leaching and migration of radioactivity from nepheline syenite-waste glasses buried below the water table at Chalk River, Ontario. Sampling in 1971 showed that the ^{90}Sr front in sandy soil had reached 33 m. Since the leach rate from the glass blocks has been constant for several years, the plume size has reached a steady state.

Himes and Shufeldt (1970) investigated the effects of soil organics on ^{90}Sr migration through soils. Thirty 0.002-acre soil microplots were delineated and 21.64 μCi ^{90}Sr added to the surface of each. Facilities were in place to collect runoff water and leachates at 40 cm depth, and ^{90}Sr was found in the leachate. The decreasing order of effectiveness of ^{90}Sr removal by organic compounds on the quantity of ^{90}Sr adsorbed by most soils was phytic acid > glucuronic acid > citric acid > pectic acid > pyrocatechol > glycine > dextrose, as shown in equilibrium experiments. Adsorption of ^{90}Sr by soils high in organic matter treated with HF-HCl solution to remove clay minerals showed that methylation with diazomethane decreased the total quantity of ^{90}Sr adsorbed. Saponification, acetylation and remethylation also altered the amount of ^{90}Sr retained on the soil. The ^{90}Sr contained in plant residues leached through 30 cm soil columns at a slow but measurable rate with applications of distilled water. Drying of soils containing ^{90}Sr at 105°C before extraction increased the fraction of water soluble ^{90}Sr that could be extracted.

Work on the long-term migration of fission products from the natural reactor site at Oklo (Brookins, 1976) indicated that strontium had partially migrated from the reactor vicinity in the past 1.8 billion years.

Laboratory Studies --

Nishita et al. (1956) studied the general extraction of radionuclides by water leaching, by exchange with 1N ammonium acetate and remaining in the soil or clay mineral. In both the soils and clays (bentonite, kaolinite) ^{90}Sr was prominent in the water soluble and cation exchangeable fractions. It showed the least tendency to remain in the soil or clay.

Orcutt et al. (1956) examined hydraulic and ion exchange phenomena as related to the underground movement of radiostrontium. Ion exchange reduced the linear velocity of the radionuclide front in relation to the liquid front. If the solid media are selective for a radionuclide, the radionuclide concentration front becomes sharp. The front becomes wider with distance traveled if the radionuclide selectivity is unfavorable. The latter condition also will occur if the waste velocity is too fast to allow instantaneous equilibrium between exchanger and the radionuclide at the concentration front.

Another article by Orcutt et al. (1957) includes experimental work on ion exchange in columns and its theoretical treatment. Several theories are presented that quantitatively describe hydraulic dispersion, ion exchange equilibria and ion exchange kinetics as they apply to the movement of radionuclides through natural porous media. In the opinion of the authors, the theoretical models, used in conjunction with field tests, served to reduce the uncertainties of ground disposal operations.

Spitsyn et al. (1960) emphasized again the ease of migration of strontium in the soil. A well was drilled and the migration of fission products was followed in the soil at a field site. At the site, up to 50 ml/l of Ca^{+2} in the groundwater caused the initial migration rate of strontium to be about 6 cm/day, practically the same speed as the groundwater. Drilling 15 months later showed that strontium contamination had spread to 6 m distance from the injection point, and that the radiostrontium migration rate was 1.1 to 1.3 cm/day compared to 6 cm/day water velocity.

A mathematical model of strontium movement in soils based on the laboratory work of Miller and Reitemeier (1957) was proposed by Thornthwaite et al. (1960). Miller and Reitemeier showed strontium distribution curves for Norfolk fine sandy loam, Miami silt loam, Huntley clay loam and Fort Collins silt loam after the application in cycles of up to three solutions (deionized water, 0.005N $CaCl_2$, 0.005N NaCl) at rates of 30 and 300 in. The strontium in the sandy soil moved farther than in the other three soils.

To describe these distributions, Thornthwaite et al. (1960) set up a model that relates leaching efficiency (cycles/in.) to soil cation exchange capacity. The model was used on a New York soil to compute the distributions of ^{90}Sr from fallout and compare the results to measured values. The comparison showed good agreement.

A study of the influence of climatic and hydrologic factors on the movement of strontium through the upper layers of soil was completed by Mather and Nakamura (1961). Strontium fallout moved through the upper part of the soil profile at a rate determined by the volume of leaching solution and the chemical and cation exchange properties of the soil and soil solution. A mathematical model was devised that allows computation of strontium movement in the soil. To use the model, values are needed for the initial strontium concentration, leaching solution volume and leaching efficiencies (cycles/in.). The leaching efficiency varied from high values in most regions to low values in dry regions for soils of the same texture. Leaching efficiency is related to moisture index. Tables and monograms were prepared to permit determination of leaching efficiency from readily available climatic data.

Jacobs (1963) reviewed an earlier paper (Jacobs, 1960) and a paper by Bovard and Grauby (1960) on retention of radiostrontium by soils. Bovard and Grauby made laboratory and field studies of the downward migration of ^{90}Sr-^{90}Y in undisturbed soils. The recovered solution was analyzed and the exposed block of soil autoradiographed after the experiment. The experimental results represented a qualitative description of the nature of the soil and system hydrodynamics. The use of a water tracer was suggested by Jacobs to obtain groundwater velocities. If heterogeneities are not severe, and flow conditions are fairly constant, the groundwater velocities and a time transformation term for radionuclide adsorption would provide a quantitative site evaluation.

Miller and Reitemeier (1963) studied leaching of strontium with applications of 76.2 cm and 762 cm of distilled water, 0.005N NaCl and 0.005N $CaCl_2$ solutions to columns containing soils contaminated with strontium-90. The $CaCl_2$ solution produced the greatest movement and the deionized water the least. The maximum distance the strontium moved with 30 in. of water was 1.3 in., and with 300 in. of water the distance moved was 4.3 in. Movement was greatest in the Norfolk loamy sand.

Some associated K values for the Mol soils are listed in Table 3-85 (Baetsle et al., 1964), where K is a measure of the velocity of strontium through the soil relative to groundwater velocity. Mol sand was almost pure silica.

TABLE 3.85. K VALUES OF STRONTIUM IN THE SATURATED SUBSOILS AT MOL, BELGIUM (BAETSLE ET AL., 1964). K IS DEFINED ON PAGE 2-30.

Soil Type	K	
	pH 7	pH 3
Mol Sand	5	1
Perturbed Profile	48	1
Mol Sand & Eolian Sand	525	-
Mol Sand & Lignite	570	-
Mol Sand	6	1
Mol Sand	7	1
Mol Sand	3	1
Mol Sand	4	1
Mol Sand	3	1
Mol Sand	6	1

The strontium Kd values and associated relative strontium velocities through the Houthulst clays at pH 3 are given in Table 3-86. Houthulst is located in western Belgium about 40 km from the North Sea. The strontium Kd values are somewhat higher for the clay but still much less than cesium. Cesium K averages 1000 while the strontium K averages 100.

TABLE 3-86. STRONTIUM DISTRIBUTION COEFFICIENTS AND RELATIVE MIGRATION RATES IN HOUTHULST CLAYS AT pH 3 (BAETSLE ET AL., 1964)

Core Well I

Depth, m	Kd, ml/g	K	Depth, m	Kd, ml/g	K
0-1	7.2	24	10-11	21.8	74
1-2	10.6	36	11-12	27.5	93
2-2.5	14.1	48	12-13	30.7	102
2.5-3	9.4	32	13-14	33.5	112
3-4	--	--	14-15	33.5	112
4-5	11.8	40	15-16	31.8	107
5-6	13.9	47	16-17	31.8	107
6-7	15.8	54	17-18	34.0	114
7-8	19.4	66	18-19	32.6	110
8-9	17.3	59	19-20	31.5	106
9-10	20.2	68			

Core Well II

0-1	--	--	10-11	30	101
1-2	3	11	11-12	30	101
2-3	5	18	12-13	28	95
3-4	18	61	13-14	29	98
4-5	18	61	14-15	31	104
5-6	23	78	15-16	31	104
6-7	29	98	16-17	29	98
7-8	31	104	17-18	31	104
8-9	16	54	18-19	31	104
9-10	29	98	19-20	31	104

Polyakov et al. (1969) determined the diffusion coefficients of strontium in three soils. The coefficients varied from 0.6 x 10^{-7} to 20 x 10^{-7} cm^2/sec. These authors pointed out that diffusion coefficients vary with the soil type and probably change appreciably within the same soil. Prokhorov (1962) had shown earlier that the diffusion coefficient in soil varied with the soil/water content. In the majority of the cases, however, except for the very long-lived radionuclides and very slow flow velocities, diffusion does not contribute greatly to radionuclide migration.

According to Schulz (1965), the radionuclides showing a degree of mobility include those of strontium. The amounts and kinds of competing cations have a marked effect on soil profile distribution as shown by the effects of comparable concentrations of NaCl and $CaCl_2$ on redistribution of ^{90}Sr down the soil profile. $CaCl_2$ moves the strontium more readily than NaCl, and the more concentrated the $CaCl_2$, the more rapid and further the strontium movement.

Nishita and Essington (1967) continued work on leaching strontium from soil columns. All soils showed that movement by water leaching resulted in more rapid movement than strontium only by ruthenium.

Carlile and Hajek (1967) reported an example of physical transport of strontium. About 0.1% of the ^{85}Sr was found in the first effluent from N-Area soil columns (2 cm diameter by 40 cm in length). Up to 1% random leakage of strontium was reported until 5 column volumes of Columbia River water had passed through the soil. Then leakage fell to below detection limits (10^{-3}%). Columbia River water has an annual mean pH of about 7.8, a mean $CaCO_3$ hardness of 69 mg/l and a mean total dissolved solids of 119 mg/l. Effluent samples were centrifuged at high speeds, treated with H_2O_2 to destroy organic material and recentrifuged. Fifty to 75% of the activity in the leaked effluent was removed. Hydrogen peroxide treatment did not affect removal of strontium by centrifugation, indicating that an organic material was not involved. Leaching a soil system with low ionic strength river water containing trace radionuclides had the result of dispersing the soil colloids on which much of the ^{85}Sr were adsorbed. Column breakthrough was immediate until the dispersed colloids were flushed from the column. Preceding the contaminated river water by a preleach of noncontaminated river water flushed the dispersed colloids and prepared the soil for use. Adding other ions to the system could have accomplished the same thing, but would have competed with adsorption of strontium.

Brendakov et al. (1969) followed the average displacement of ^{90}Sr from a Chestnut soil. The ^{90}Sr was amended to the soil in the field and sampled at yearly intervals. Two years after amendment, the average displacement distance from the surface was 11 mm and 5 years after amendment, 16 mm.

The average displacement was defined as:

$$\overline{X} = \frac{\Sigma pixi}{\Sigma pi}$$

where

pi = fractional % of the radionuclide in a layer (3 mm thickness)
xi = the depth of the layer.

There was little difference in $\overline{X}$ for any of the radionuclides used in the experiment.

Chelation and movement of strontium in a calcareous soil were evaluated in columns of Mohave sandy loam soil (Fuller and L'Annunziata, 1969). The displacement of ^{89}Sr from the soil columns was 19, 38, 44, 47, and 81% in the order HEEDTA < DCyTA < EDTA ≤ EGTA < DTPA. Only 5% of the ^{89}Sr was removed from the soil with no complexing agents in the leaching solution. The radiostrontium existed in the leachate as a negative complex. Any natural organic chelating agents in the soil did not influence radiostrontium movement.

Four soils varying greatly in organic matter content, cation exchange capacity and texture were studied by Juo and Barber (1970) for their strontium retention characteristics. The adsorption of strontium by soils increased with increasing pH within the pH range 4 to 8. Saturating cations had some effect on strontium adsorption, with influence in the order Na>K>Mg>Ca>Ba>H. As the pH increased, an increasing fraction of the adsorbed strontium became nonexchangeable with ammonium acetate. The nonexchangeable portion of the strontium is probably tied up by soil organics and is permanently fixed under favorable pH conditions. In a higher pH environment, a larger portion of the strontium in solution was present as soluble strontium chelates or complexes.

Varga and Jacobs (1970) examined how the strontium from dissolved (Ca, ^{85}Sr) CO_3 moved through a mineral exchange system as represented by a vermiculite column. The (Ca, ^{85}Sr) CO_3 was precipitated on the top of the column by mixing 50 ml of 0.4M NaOH, 50 ml of 0.7M NaCl, ^{45}Ca, ^{85}Sr, 1 ml 1M $NaHCO_3$

and 1 ml 1M $Ca(NO_3)_2$, and allowing the mixture to stand 1 hr. An HCl solution was then used to leach the strontium-contaminated calcite precipitated on top of the column. The behavior of the released calcium (traced with ^{45}Ca) and strontium were very similar. Less than 1% of the ^{45}Ca and ^{85}Sr on top of the column appeared in the effluent prior to acid addition, and no significant activity was found in the effluent until breakthrough of the acid front occurred. The release of calcium and strontium from the system was directly related to the amount of acid added in the leaching process.

Summary

Most of the strontium chemical compounds for which data are available are very soluble (Figure 3-22). Only in highly alkaline soils could $SrCO_3$ control strontium activity in solutions. Strontium in solution is expected to be predominantly present as Sr^{2+} (Figure 3-23) and to be exchangeable on soils. Laboratory studies show that ion exchange is the principal mechanism of strontium adsorption by soils and rocks (McHenry, 1955, 1958; Rhodes and Nelson, 1957; Klechovsky et al., 1958; Prout, 1958, 1959; Baker and Beetem, 1961; Cohen and Gailledreau, 1961). Strontium Kd values are usually directly correlated with cation exchange capacity of the soil or rock, but not invariably (McHenry, 1958). A direct correlation between solution pH and strontium Kd has also been reported (Rhodes, 1957; Prout, 1958, 1959; Baetsle et al., 1964; Juo and Barber, 1970), which suggests hydrogen ion competition with Sr^{2+} for exchange sites. Strontium Kd values fall rapidly from 100 to 200 ml/g or more in low ionic strength salt solutions to less than 5 ml/g in high ionic strength salt solutions (Rhodes, 1957; Serne, 1973). Strontium and calcium most readily replace trace strontium (Kokotov et al., 1961, 1962; Schulz, 1965) and cause strontium radioisotopes to migrate rapidly when present in groundwater with the strontium (Spitsyn et al., 1960). Low pH also results in a relatively high strontium migration velocity in groundwater (Parsons, 1963; Baetsle et al., 1964) with the strontium and groundwater velocity identical at pH 3. Calcium competition is the probable cause of the 90% soluble strontium migration from the lagoons of the Nuclear Fuel Services plant (Magno et al., 1970), although strontium also migrates on soil particulates (Carlile and Hajek, 1967). The many strontium Kd values determined by Berak (1963) demonstrated that secondary minerals such as clays and zeolites are much better strontium adsorbers and are more selective for strontium from solutions containing strontium and calcium than are the primary minerals such as quartz, feldspars and pyroxenes. Another mechanism for strontium removal from solution is its coprecipitation with calcite (Jenne and Wahlberg, 1968; Varga and Jacobs, 1970) or adsorption during phosphate or oxalate replacement of carbonate in calcite (McHenry, 1958; Ames, 1958). Strontium organic complexes are known that result in a measure of strontium fixation (Mortensen and Marcusiu, 1963) or enhanced migration rates (Himes and Shufeldt, 1970).

References

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Ames, L. L., Jr. 1959. The Genesis of Carbonate Apatites, Economic Geology. 54:829-841.

Ames, L. L., Jr., J. R. McHenry, and J. F. Honstead. 1958. The Removal of Strontium from Wastes by a Calcite - Phosphate Mechanism. IN: Proc. 2nd UN Int. Conf. PUAE. 18:76.

Amphlett, C. B. and L. A. McDonald. 1956. Equilibrium Studies on Natural Ion-Exchange Minerals. I:Caesium and Strontium. J. Inorg. Nucl. Chem. 2:403-414.

Angelo, C. G., N. C. Goldberg, V. J. Janzer, and W. A. Beetem. 1962. Summary of Kd's for Fission Products Between Ground Water and Basaltic Rocks. IN: Geology of the U18a Site, Buckboard Mesa, NTS. Part VI. U.S.G.S. Report Project Danny Boy, WT 1828, pp. 66-81.

Baetsle, L. and P. Dejonghe. 1962. Investigations on the Movement of Radioactive Substances in the Ground. Part III: Practical Aspects of the Program and Physicochemical Considerations. IN: Proc. Conf. Ground Disposal of Radioactive Wastes, 2nd, Chalk River, Canada, September 1961. J. M. Morgan, D. K. Jamison, and J. D. Stevenson (eds.) TID-7628, pp. 198-210.

Baetsle, L., P. Dejonghe, W. Maes, and P. Staner. 1963. Present Status of the Study Program on the Movement of Radioelements in the Soil at Mol. EURAEC-416.

Baetsle, L. H., P. Dejonghe, W. Maes, E. S. Simpson, J. Souffriau, and P. Staner. 1964. Underground Radionuclide Movement. EURAEC-703.

Baker, J. H. and W. A. Beetem. 1961. Distribution Coefficients for Adsorption of Carrier-Free Cesium, Strontium, and Iodine by Sample from the Vicinity of Cape Thompson, NW Alaska, U.S.G.S. Tech Letter Chariot-1.

Beetem, W. A., V. J. Janzer, C. G. Angelo, and M. C. Goldberg. 1962. Summary of Distribution Coefficients for Fission Products Between Ground Water and Granite Rocks, Climax Stock, NTS. U.S.G.S. Technical Letter NTS-13.

Benson, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Berak, L. 1963. The Sorption of Microstrontium and Microcesium on the Silicate Minerals and Rocks. UJV-528-63.

Bovard, P. and A. Grauby. 1960. A Study of the Aptitude of Soils Under Natural Conditions to Retain Radiostrontium. AEC-tr-5453.

Brendakov, V. F., A. V. Dibtseva, V. I. Svishcheva, and V. N. Churkin. 1969. Vertical Distribution and Evaluation of the Mobility of Fission Products in Certain Soil Types of the Soviet Union. AEC-tr-7030, pp. 152-170.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Carlile, B. L. and B. F. Hajek. 1967. Soil Radionuclide Adsorption and Particulate Filtration in an N-Area Soil. BNWL-CC-995.

Carrigan, P. H., Jr., R. J. Pickering, T. Tamura, and R. Forbes. 1967. Radioactive Materials in Bottom Sediment of Clinch River: Part A, Investigations of Radionuclides in Upper Portion of Sediment. ORNL-3721, Suppl. 2A.

Cerrai, E., M. G. Mezzadri and C. Triulzi. 1969. Sorption Experiments of Strontium, Cesium, Promethium, and Europium on Marine Sediment Samples. Energia Nucleare. 16:378-385.

Cohen, P. and C. Gailledreau. 1961. Preliminary Investigations of the Adsorption of Radiostrontium in Saclay Soil. Three-Component System. TID-7621, pp. 90-99.

Dlouhy, Z. 1967. Movement of Radionuclides in the Aerated Zone. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/18, pp. 241-249.

Essington, E. H. and W. E. Nork. 1969. Radionuclide Contamination Evaluation - Milrow Event. NVO-1229-117.

Evans, E. J. 1958. Chemical Investigations of the Movement of Fission Products in Soil. CRER-792.

Fuller, W. H. and M. F. L'Annunziata. 1969. Movement of Algal- and Fungal-Bound Radiostrontium as Chelate Complexes in a Calcareous Soil. Soil Science. 107:223-30.

Gardner, K. and O. Skulberg. 1964. Sorption Phenomena of Radionuclides to Clay Particles in River Water. Int. J. Air Wat. Poll. 8:229-241.

Goldberg, M. C., V. J. Janzer, C. G. Angelo, and W. A. Beetem. 1962. The Effect of Sodium Ion Concentration on Distribution Coefficients for Tuffs from NTS. U.S.G.S. Technical Letter NTS-16.

Hajek, B. F. and L. L. Ames, Jr. 1968. Trace Strontium and Cesium Equilibrium Distribution Coefficients: Batch and Column Determinations. BNWL-SA-843.

Hawkins, D. B. and H. L. Short. 1965. Equations for the Sorption of Cesium and Strontium on Soil and Clinoptilolite. IDO-12046.

Himes, F. L. and R. Shufeldt. 1970. Influence of Some Organic Compounds on the Movement of Sr^{90} in Soils. COO-414-11.

Izrael, Yu.A. and F.Ya. Rovinskii. 1970. Hydrological Uses of Isotopes Produced in Underground Nuclear Explosions for Peaceful Purposes. UCRL-Trans-10458.

Jackson, D. D. 1976. Radiochemical Studies for the Nuclear Chemical Mining of Copper. UCRL-52025.

Jacobs, D. G. 1960. Strontium Movement in the Soil. Nuclear Safety. 2:63-65.

Jacobs, D. G. 1963. Movement of Radionuclides Through the Ground. Nuclear Safety. 5:109-115.

Janzer, V. J., M. C. Goldberg, C. G. Angelo and W. A. Beetem. 1962. Summary of Distribution Coefficients for Fission Products Between Ground Water and Rocks from Project Gnome. IN: Hydrologic and Geologic Studies for Project Gnome. Part IV. U.S.G.S.

Jenne, E. A. and J. S. Wahlberg. 1968. Role of Certain Stream - Sediment Components in Radioion Sorption. U.S.G.S. Professional Paper 433-F.

Juo, A. S. R. and S. A. Barber. 1970. The Retention of Strontium by Soils as Influenced by pH, Organic Matter and Saturated Cations. Soil Science. 109:143-148.

Kaufman, W. J. 1963. An Appraisal of the Distribution Coefficient for Estimating Underground Movement of Radioisotopes. HNS-1229-21.

Klechkovsky, V. M., L. N. Sokdova, and G. N. Tselishcheva. 1958. Sorption of Microquantities of Strontium and Cesium in Soil. IN: Proc. UN Inter. Conf. Peaceful Uses of Atomic Energy, 2nd, Geneva, September 1-13, 1958. 18:486-493.

Kokotov, Yu. A. and R. F. Popova. 1962. Sorption of Long-Lived Fission Products by Soils and Argillaceous Minerals III: Selectivity of Soils and Clays Toward ^{90}Sr Under Various Conditions. Sov. Radiochem. 4:292-297.

Kokotov, Yu. A., R. F. Popova, and A. P. Urbany. 1961. Sorption of Long-Lived Fission Products on Soils and Clay Minerals. Radiokhimya. 3:199-206.

Lomenick, T. F., D. G. Jacobs and E. G. Struxness. 1967. The Behavior of Strontium-90 and Cesium-137 in Seepage Pits at ORNL. Health Physics. 13:897-905.

Magno, P., T. Reavey, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Mather, J. R. and J. K. Nakamura. 1961. The Climatic and Hydrologic Factors Affecting the Redistribution of Sr^{90}. AFOSR-1623.

Mawson, C. A. 1956. Waste Disposal into the Ground. Proc. of the Inter. Conf. on the Peaceful Uses of Atomic Energy. 9:676-678.

McHenry, J. R. 1955. Adsorption and Retention of Strontium by Soils of the Hanford Project. HW-34499.

McHenry, J. R. 1958. Ion Exchange Properties of Strontium in a Calcareous Soil. Soil Science Society America, Proceedings. 22:514-518.

Mercer, B. W. 1966. Adsorption of Trace Ions from Intermediate Level Radioactive Wastes by Ion Exchange. BNWL-180.

Mercer, B. W. 1967. Ion Exchange Equilibria of Trace Cesium 137 and Strontium-85 in Multicomponent Systems. BNWL-SA-1173.

Merritt, W. F. 1967. Permanent Disposal by Burial of Highly Radioactive Wastes Incorporated Into Glass. IN: Disposal of Radioactive Wastes Into the Ground. IAEA, Vienna, pp. 403-408.

Merritt, W. F. 1976. The Leaching of Radioactivity from Highly Radioactive Glass Blocks Buried Below the Water Table: Fifteen Years of Results. AECL-5317.

Miller, J. R. and R. F. Reitemeier. 1957. Rate of Leaching of Radiostrontium Through Soils by Simulated Rain and Irrigation Water. U.S. Dept. Agr. ARS Research Rept. No. 300.

Miller, J. R. and R. F. Reitemeier. 1963. The Leaching of Radiostrontium and Radiocesium Through Soils. Soil Sci. Soc. Am. Proc. 27:141-144.

Mortensen, J. L. and E. C. Marcusiu. 1963. Fission Product-Soil Organic Matter Complexes: I. Strontium-90 (Yttrium-90) in Water Extracts and HCl Hydrolysates of Soil. Soil Sci. Soc. Amer. Proc. 27:653-656.

Nishita, H., B. W. Kowalewsky, A. J. Steen, and K. H. Larson. 1956. Fixation and Extractability of Fission Products Contaminating Various Soils and Clays. Soil Science. 81:317-326.

Nishita, H. and E. H. Essington. 1967. Effect of Chelating Agents on the Movement of Fission Products in Soils. Soil Science. 103:169-176.

Nork, W. E. and P. R. Fenske. 1970. Radioactivity in Water - Project Rulison. NVO-1229-131.

Nork, W. E., E. J. Forslow, and E. H. Essington. 1971. Radioactivity in Water, Central Nevada Test Area. NVO-1229-175.

Orcutt, R. G., I. Naor, G. Klein and W. J. Kaufman. 1956. Hydraulic and Ion-Exchange Phenomena in the Underground Movement of Radiostrontium. TID-7517 (Pt. 1), pp. 191-211.

Orcutt, R. G., M. N. E. Rifai, G. Klein, and W. J. Kaufman. 1957. Underground Movement of Radioactive Wastes Presented at Nuclear Engineering and Science Congress; Philadelphia, Pennsylvania, March 11, 1957.

Parker, V. B., D. D. Wagman, and W. H. Evans. 1971. Selected Values of Chemical Thermodynamic Properties. Tables for the Alkaline Earth Elements (Elements 92 through 97) in the Standard Order of Arrangement. NBS Technical Note 270-6.

Parsons, P. J. 1961. Movement of Radioactive Waste Through Soil. 3. Investigating the Migration of Fission Products from high-Ionic Liquids Deposited in Soil. CRER-1018.

Parsons, P. J. 1963. Migration from a Disposal of Radioactive Liquid in Sands. Health Physics. 9:333-342.

Polyakov, Yu. A., V. F. Gol'tsov, and V. G. Grakovskiy. 1969. The Diffusion of Strontium-90 in Soils. AEC-tr-7030, pp. 14-25.

Prokhorov, V. M. 1962. Diffusion of Strontium-90 in Soil and Sand. Radiokhimiya. 4:205-211.

Prout, W. E. 1958. Adsorption of Radioactive Wastes by Savannah River Plant Soil. Soil Science. 86:13-17.

Prout, W. E. 1959. Adsorption of Fission Products by Savannah River Plant Soil. DP-394.

Rhodes, D. W. 1957. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Science Society of America, Proceedings. 21:389-392.

Rhodes, D. W. and J. L. Nelson. 1957. Disposal of Radioactive Liquid Wastes from the Uranium Recovery Plant. HW-54721.

Routson, R. C. 1973. A Review of Studies on Soil-Waste Relationships on the Hanford Reservation from 1944 to 1967. BNWL-1464.

Schmalz, B. L. 1972. Radionuclide Distribution in Soil Mantle of the Lithosphere as a Consequence of Waste Disposal at the National Reactor Testing Station. IDO-10049.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Sokol, D. 1970. Groundwater Safety Evaluation - Project Gasbuggy. PNE-1009.

Sorathesn, A., G. Bruscia, T. Tamura, and E. G. Struxness. 1960. Mineral and Sediment Affinity for Radionuclides. CF-60-6-93.

Spitsyn, V. I., V. D. Balukova, A. F. Naumova, V. V. Gromov, F. M. Spiridonov, E. M. Vetrov, and G. I. Gravfov. 1958. A Study of the Migration of Radioelements in Soils. IN: Proc. Second Annual U.N. Conf. Peaceful Uses of Atomic Energy. 18:439-448.

Spitsyn, V. I., V. D. Balukova, V. V. Gromov, S. I. Zakharov, B. P. Zhagin and F. M. Spiridonov. 1960. Sorption Regularities in Behavior of Fission-Product Elements During Filtration of Their Solutions Through Ground. IN: Disposal of Radioactive Wastes. II:429-435.

Spitsyn, V. I. and V. V. Gromov. 1958. A Study of the Systematic Adsorption of Radioactive Strontium by Montmorillonite and Its Fixation by Roasting. Soviet Atomic Energy. 5:1341-1347.

Stead, F. W. 1963. Tritium Distribution in Ground Water Around Large Underground Fusion Explosions. Science. 142:1163-1165.

Stead, F. W. 1964. Distribution in Groundwater of Radionuclides from Underground Nuclear Explosions. IN: Proc. 3rd Plowshare Symp. TID-7695.

Tamura, T. 1964. Reactions of Cesium-137 and Strontium-90 with Soil Minerals and Sesquioxides. ORNL-P-438.

Tamura, T. and E. G. Struxness. 1963. Reactions Affecting Strontium Removal from Radioactive Wastes. Health Physics. 9:697-704.

Thornthwaite, C. W., J. R. Mather, J. K. Nakamura. 1960. Movement of Radiostrontium in Soils. Science. 131:1015-1019.

Turekian, K. K. and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Bull. Geol. Soc. Am. 72:175.

Varga, J. A. and D. G. Jacobs. 1970. Dissolution of Calcium-Strontium Carbonate and Its Subsequent Movement in the Ground. ORNL-TM-3130.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.

Wahlberg, J. S., J. H. Baker, R. W. Vernon, and R. S. Dewar. 1965. Exchange Adsorption of Strontium on Clay Minerals. U.S.G.S. Bulletin 1140-C.

Wahlberg, J. S. and R. S. Dewar. 1965. Comparison of Distribution Coefficients for Strontium Exchange from Solutions Containing One and Two Competing Cations. U.S.G.S. Bulletin 1140-D.

Wilding, M. W. and D. W. Rhodes. 1963. Removal of Radioisotopes from Solution by Earth Materials from Eastern Idaho. IDO-14624.

TECHNETIUM

Natural Soil and Rock Distributions

According to Boyd and Larson (1956), technetium occurs in most abundance in molybdenite (MoS_2), a common molybdenum ore, as shown in Table 3-87. The technetium content of all materials except pitchblende is of secondary origin, formed by the action of cosmic radiation on molybdenum, ruthenium or niobium. The ^{99}Tc in pitchblende is a product of ^{238}U spontaneous fissioning. Not everyone accepts the existence of the natural ^{99}Tc as having been proven (see Handbook of Chemistry and Physics, 57th Edition, p. B-50).

TABLE 3-87. TECHNETIUM CONTENT OF SOME NATURAL MATERIALS (BOYD AND LARSON, 1956)

Material	Tc, g/kg	Determination Method
Molybdenite, Climax, CO	$<4 \times 10^{-10}$	Spectroscopic
Molybdenite, NV	$<1.5 \times 10^{-9}$	Spectroscopic
Molydenite, Miami, AZ	$<1.8 \times 10^{-7}$, 8.3×10^{-11}, 1.3×10^{-11}	Activation
Molybdenite, NV	1.3×10^{-10}	Activation
Osmium-iridium concentrate	$<1.6 \times 10^{-8}$	Spectroscopic
Yttrotantalite, West Africa	$<6 \times 10^{-11}$	Mass Spec.
Iron-nickel Meteorite	$<4.5 \times 10^{-10}$	Spectroscopic
$KReO_4$, pure	$<8 \times 10^{-9}$	Spectroscopic
Pitchblende (∿50% uranium)	2.5×10^{-10} ^{99}Tc (Ashizawa and Kuroda, 1957)	

Brief Chemistry

There are 16 isotopes and 6 isomers of technetium presently known (Lavrukhina and Pozdnyakov, 1970). Several technetium isotopes are obtained by the fissioning of nuclear fuels of uranium in the reactor. The fission product technetium isotopes and their yields include: ^{99}Tc, 6.06%; ^{101}Tc, 5.6%; ^{102}Tc, 4.3%; ^{103}Tc, 3.0%; ^{104}Tc, 1.8%; ^{105}Tc, 0.9%; ^{107}Tc, 0.19% (Katcoff, 1958). According to Boyd (1959), the technetium content of first cycle Purex waste is 41 mg/l. Only ^{99}Tc is long half-lived (2.12×10^5 years) of the several fission product technitium isotopes, and hence a potential hazard.

Technetium exists in valence states from (VII) to (-I). The most stable state in aqueous solutions is heptavalent, usually corresponding to the TcO_4^- (pertechnetate) ion, which other valences encountered chiefly in complex compounds. The ionic radius of Tc^{+7} is 0.56 Å, while its geochemical relative, Re^{+7}, is 0.45 Å. The corresponding radius of the solvated TcO_4^- ion is 4.6 Å (Smith et al., 1953). In weakly acid, neutral and alkaline solutions, Tc(IV), the second most stable state of technetium, is oxidized by atmospheric oxygen to Tc(VII). The solubility of $KTcO_4$ in water at 20°C is 21.3 g/l (Busey and Larson, 1958). Technetium (IV) and Tc(V) form halogen complexes such as $(TcCl_6)^{-2}$, and Tc(II), (III) and (V) form diarsine complexes and cyanide complexes.

Solid Phase and Solution Equilibria

Baes and Mesmer (1976) reported that technetium (VII) forms strong peracids (HMO_4), and that its oxides are very soluble. No information is available concerning the soluble complexes of technetium or the solubility of its salts (Pourbaix, 1966). Pertechnetate ion, TcO_4^-, is the most stable species of the element in aqueous solutions (Boyd, 1959).

Experimental Adsorption Results

Wildung et al. (1975) used a batch equilibrium technique to determine pertechnetate ion adsorption on soils. The range of the 22 soil type properties used in the study are given in Table 3-88. The Kd values for pertechnetate ranged from 0.007 to 2.8. The Kd values were positively correlated with soil organic carbon content and negatively correlated with soil pH. The positive charge on soil organic colloids is probably an important factor in technetium adsorption by soils. The soil carbon-pertechnetate ion removal correlation was the only one significant at the 1% confidence level. Cation exchange capacity-pertechnetate ion removal also was positively correlated but at a 5% confidence level. Negatively correlated at the 5% confidence level was pH-pertechnetate ion removal, probably because as pH decreases, positive charge increases with decreased ionization of acidic groups of soil organic colloids and increased protonation of basic groups. A regression equation was given for pertechnetate distribution coefficient determination within the range of significant independent variables. This was $Y_1 = 0.08X_3 - 0.09X_4$, where Y_1 is the pertechnetate distribution coefficient (based on the ranges shown in Table 3-88), X_3 is the soil organic carbon content and X_4 is the soil-solution pH. The soil silt content (X_1) and clay content (X_2) correlations with Kd were not statistically significant at the 5% confidence level and did not, therefore, appear in the regression equation.

TABLE 3-88. RANGE OF PROPERTIES OF 22 SURFACE SOILS USED IN THE PERTECHNETATE ADSORPTION STUDIES (WILDUNG ET AL., 1975)

Cation Exchange Capacity, meq/100 g	pH	wt% CO_3	wt% Organic C	wt% Sand	wt% Silt	wt% Clay
5.5-90.0	3.6-8.9	0-6.5	0.23-28.8	14.1-73.1	17.6-58.0	3.8-46.6

Gast (1975) studied several Minnesota soils and their abilities to adsorb pertechnetate ions. The soil characteristics are outlined in Table 3-89. From 2 to 5 weeks of contact time between soil and solution were required for equilibrium to be established. Nicollet C and Zimmerman soils, both low in organic carbon content, adsorbed very little ^{99}Tc, while up to 98% of the technetium was adsorbed from solution by the remaining soils corresponding to a ^{99}Tc Kd value of 857.5 ml/g. When the organic carbon was removed by hydrogen peroxide treatment from two soils originally high in carbon content, the adsorption of technetium was greatly reduced. Gast also mentioned that anaerobic conditions prevailed in the soil-solution environment which may have led to the precipitation of technetium heptasulfide, rather than technetium removal by adsorption processes.

TABLE 3-89. PROPERTIES OF SOILS USED IN THE TECHNETIUM ADSORPTION STUDIES (GAST, 1975)

Soil	wt% Sand	wt% Silt	wt% Clay	pH, H_2O	Organic C, wt%	$CaCO_3$, wt%	% Fe_2O_3	C.E.C., meq/100 g
Bearden	9.1	63.7	27.2	7.68	5.39	16.29	0.09	16.9
Hegne	1.9	37.6	60.5	8.00	2.20	12.79	0.29	36.1
Hibbing	3.3	79.5	17.2	5.48	2.29	--	1.40	11.3
Nicollet A	24.4	42.9	29.7	5.91	2.39	--	0.86	19.3
Nicollet C	23.9	48.6	27.5	8.40	0.12	15.21	1.35	15.7
Omega	61.5	30.7	7.9	7.87	1.26	1.21	1.20	6.0
Bergland	14.0	25.1	60.9	6.35	5.67	--	2.39	32.3
Arveson	47.1	24.6	28.3	7.70	2.80	15.58	0.21	14.9
Waukegan	10.0	69.2	20.7	6.25	2.36	--	1.03	15.1
Zimmerman	69.4	24.9	5.7	5.74	0.80	--	0.47	2.7
Peat	--	--	--	7.83	45.95	7.58	0.40	50.9

Routson et al. (1976, 1977) determined distribution coefficients on technetium with Washington and South Carolina soils. Soil properties are given in Table 3-90. The organic carbon content was not given. The technetium Kd values obtained were very low, as seen in Table 3-91, when competing bicarbonate ions were present in the system. All Kd values were essentially zero.

TABLE 3-90. PROPERTIES OF SOIL SAMPLES (ROUTSON ET AL., 1977)

Soil	$CaCO_3$, mg/g	wt% Silt	wt% Clay	CEC, meq/100 g	pH, H_2O
Washington	0.8	10.1	0.5	4.9	7.0
South Carolina	<0.2	3.6	37.2	2.5	5.1

TABLE 3-91. TECHNETIUM Kd AS A FUNCTION OF $NaHCO_3$ CONCENTRATION FOR A SOUTH CAROLINA SOIL CHARACTERIZED IN TABLE 3-90 (ROUTSON ET AL., 1977)

$NaHCO_3$, M	Average Kd, ml/g
0.002	0.019 ± 0.06
0.008	0.0 ± 0.01
0.020	0.0 ± 0.01
0.200	0.010 ± 0.04

Migration Results

Field Studies--

Brown (1967) traced the movement of technetium discharged to the ground near the chemical separations plant at Hanford via an extensive network of monitoring wells. Based on analytical results, a map of the contamination pattern at the surface of the groundwater was given for 1966 at limits defined by the 0.01 pCi $^{99}Tc/cm^3$ isoconcentration contour. The contamination pattern was very similar in shape and size to that for tritium. Technetium-99 was reported to be moving at essentially the same rate as the groundwater, and was detectable in the groundwater at below public drinking water limits all the way to the Columbia River.

Brookins (1976) pointed out that the technetium formed as a result of nuclear fission of the deposit of uranium at Oklo, Gabon, had at least partially migrated from the shale location in which it was formed.

Laboratory Studies--

Gast (1975) reported the extractability of technetium from Bergland and Arveson soils. The characteristics of these soils are given in Table 3-92. Two-gram samples of air-dried Bergland and Arveson were loaded with 0.06 μCi of ^{99}Tc. Less than 2% of the ^{99}Tc still remained in the equilibrating solution after 1 month of contact. These 2-g samples loaded with 0.06 μCi ^{99}Tc were used in the extraction studies. Twenty-five milliliters of extractant (1N NaOH or 1N $HClO_4$) were added to the 2-g samples in sequence and shaken for 24 hr with the results shown in Table 3-93.

TABLE 3-92. PROPERTIES OF BERGLAND AND ARVESON SOILS USED IN THE ^{99}Tc EXTRACTION WORK (GAST, 1975)

	wt%			Organic Carbon, %	$CaCO_3$, %	pH, H_2O	CEC, meq/100g
	Sand	Silt	Clay				
Bergland	14.0	25.1	60.9	5.67	-	6.35	32.3
Arveson	47.1	24.6	28.3	2.80	15.58	7.70	14.9

TABLE 3-93. EXTRACTABILITY OF ^{99}Tc FROM BERGLAND AND ARVESON SOILS (GAST, 1975)

Soil	Extractant	Extraction	^{99}Tc, %	Total ^{99}Tc, %
Bergland	NaOH	1	77.4±3.25	
		2	8.69±1.97	88.74±1.02
		3	1.82±0.16	
		4	0.83±0.10	
Arveson	NaOH	1	83.68±1.05	
		2	4.77±0.07	91.82±0.98
		3	2.39±0.11	
		4	0.98±0.07	
Bergland	$HClO_4$	1	11.95±0.14	
		2	6.90±0.31	26.83±0.60
		3	4.46±0.07	
		4	3.52±0.01	
Arveson	$HClO_4$	1	7.22±0.01	
		2	2.96±0.04	13.63±0.02
		3	2.16±0.04	
		4	1.30±0.01	

The concomitant removal of soil organic matter suggested that the TcO_4^- ion may be associated with it. However, Gast showed that large amounts of chloride ions (KCl) or HPO_4^{-2} from K_2HPO_4 had no significant effect on ^{99}Tc adsorption by Bergland and Arveson soils so that simple anion exchange probably was not involved in the adsorption. The low ^{99}Tc adsorption shown by low organic soils, and the effects of prior hydrogen peroxide removal of Bergland organic material on lowering the ^{99}Tc adsorption capacity, strongly suggest that the technetium is adsorbed on the soil organics. The presence of H_2S reported from certain of the adsorption experiments suggests the reduction of Tc(VII) to Tc(IV) and precipitation of Tc_2S_7 as well. The NaOH removes both adsorbed and precipitated technetium from the soil, while the perchloric acid is partially consumed by reactions with the organic fraction and is therefore not as an effective technetium removal agent as NaOH.

Summary

Pertechnetate ion, TcO_4^-, is the most stable species of technetium in aqueous solutions (Boyd, 1959). A major portion of the ion exchange capacity of soils and sediments is cation exchange capacity at the usual near-neutral pH conditions. Therefore a negatively charged TcO_4^- would hardly be exchanged, and hence show little adsorption by soils and rocks (Routson et al., 1976, 1977). Gast (1975) reported high Kd values (800 to 900) for soils with high organic matter. He also reported the presence of H_2S in his equilibrating samples, and suggested that the high Kd values were due to precipitation of technetium as Tc_2S_7 in the presence of H_2S (Kotegov, 1968). In conditions where the soil contains appreciable organic matter, the Tc(VII) may be reduced to Tc(IV) and adsorbed (Wildung et al., 1975). Tc(IV) can coprecipitate with ferric hydroxide (Anders, 1960). With the exception of some sedimentary rocks, most rocks contain very little organic matter. Hence, technetium Kd values of close to zero would normally be encountered in oxidizing conditions and in rocks and soils that are relatively low in organic matter. More study is required to determine the nature of the organic matter-pertechnetate ion reaction, and the influence of redox conditions on adsorption of technetium by soils and rocks.

References

Anders, E. 1960. The Radiochemistry of Technetium. Nuclear Sci. Ser. Nat. Acad. Sci. - Nat. Res. Council. NAS-NS 3021.

Ashizawa, F. T. and P. K. Kuroda. 1957. The Occurrence of the Short-Lived Iodine Isotopes in Natural and in Depleted Uranium Salts. J. Inorg. Nucl. Chem. 5:12-22.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Boyd, G. E. 1959. Technetium and Promethium. J. Chem. Educ. 36:3-14.

Boyd, G. E. and Q. V. Larson. 1956. Report on the Occurrence of Technetium on the Earth's Crust. J. Phys. Chem. 60:707-715.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Busey, R. H. and Q. V. Larson. 1958. Chemistry Division Annual Progress Report for Period Ending June 20, 1958. ORNL-2584.

Gast, R. G. 1975. The Behavior of Technetium-99 in Soils and Plants. Progress Report. COO-2447-1.

Katcoff, S. 1958. Fission-Product Yield from U, Th, and Pu. Nucleonics. 16:78-86.

Kotegov, K. V., O. N. Pavlov and V. P. Shvedov. 1968. Technetium. IN: Advances in Inorganic Chemistry and Radiochemistry, vol. 11, pp. 1-90, Academic Press, NY.

Lavrukhina, A. K. and A. A. Pozdnyakov. 1970. Analytical Chemistry of Technetium, Promethium, Astatine, and Francium. Translated by R. Kondor. Ann Arbor-Humphrey Science Publishers.

Pourbaix, M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, England.

Routson, R. C., G. Jansen and A. V. Robinson. 1976. ^{99}Tc, ^{237}Np, and ^{241}Am Sorption on Two Subsoils from Differing Weathering Intensity Areas. BNWL-2000. Pt. 2, pp. 50-52.

Routson, R. C., G. Jansen and A. V. Robinson. 1976. ^{241}Am, ^{237}Np, and ^{99}Tc Sorption on Two United States Subsoils from Differing Weathering Intensity Areas. BNWL-1889.

Smith, W. T., J. W. Cobble, and G. E. Boyd. 1953. Thermodynamic Properties of Technetium and Rhenium Compounds. I. Vapor Pressures of Technetium Heptoxide, Pertechnic Acid and Aqueous Solution of Pertechnic Acid. J. Am. Chem. Soc. 75:5773-5776.

Wildung, R. E., R. C. Routson, R. J. Serne, and T. R. Garland. 1975. Pertechnetate, Iodide and Methyl Iodide Retention by Surface Soils. BNWL-1950. Pt. 2, pp. 37-40.

THORIUM

Natural Soil and Rock Distributions

The content of thorium in rocks and soil is given in Table 3-94. The thorium in sedimentary rocks may be due either to the selective adsorption of thorium on clays or its retention in heavy resistate minerals such as monazite. Concentrations of thorium in metamorphic rocks are highly variable. The thorium content of igneous rocks increases from basalts to granites.

TABLE 3-94. THORIUM CONTENT OF COMMON ROCKS AND SOILS

Rock Type	Thorium Average or Range, ppm	Reference
	Igneous Rocks	
Granites	10-20	Rogers, 1964
Intermediate	2-10	Heier and Carter, 1964
Basalt and Gabbros	0.5-2	Heier and Rogers, 1963
	Sedimentary Rocks	
Shales, North America	10-15	Adams and Weaver, 1958
Bauxites	49	Adams and Richardson, 1960
Bentonites	24	Adams and Weaver, 1958
Limestones	1.1	Adams and Weaver, 1958
Sandstones	1.7	Murray and Adams, 1958
Soils	6	Vinogradov, 1959
	Metamorphic Rocks	
Marble	0.03	Pliler, 1956
Slate	7.5	Pliler, 1956
Phyllite	5.5	Pliler, 1956
Schist	7.5	Pliler, 1956
Gneiss	13.1	Billings, 1962

Thorium adsorption studies were performed by several investigators. Holland and Kulp (1954) found red clay, globigerina ooze and green clay readily adsorbed thorium. They concluded that ion exchange was the adsorption mechanism. Adams et al. (1959) suggested that thorium is concentrated by clay minerals. Up to 50 ppm thorium in the aluminum hydroxide and resistate minerals in bauxite was reported by Adams and Richardson (1960).

Brief Chemistry

There are 13 isotopes of thorium with six of them found in nature. Of the six natural thorium isotopes, five are relatively quantitatively unimportant members of the ^{238}U, ^{235}U or ^{232}Th decay series. Thorium-232 is the major isotope, with a half-life of 1.39 × 10^{10} years (Ryabchikov and Golbraikh, 1969). Thorium radionuclide data of interest in waste disposal operations are in given in Table 3-95.

TABLE 3-95. THORIUM RADIONUCLIDE DATA (RYABCHIKOV AND GOLBRAIKH, 1969)

Isotope	Half-Life	Decay Mode
^{227}Th	18.5 days	α
^{228}Th	1.913 years	α
^{229}Th	7340 years	α
^{230}Th	80,000 years	α
^{231}Th	25.5 hours	β^-
^{232}Th	1.41 x 10^{10} years	α
^{234}Th	24.1 days	β^-

Although other oxidation states of thorium are known in the laboratory, only Th(IV) is found in nature. Th(IV) is found as Th^{+4}. The atomic radius of Th^{+4} is 0.99 Å (Ahrens, 1952).

Common insoluble thorium compounds include the hydroxide, fluoride and phosphate. Soluble compounds include the chloride, nitrate and sulfate. Thorium in solution is a small, highly charged ion that undergoes extensive interaction with water and many anions. The solution chemistry of thorium is largely a study of its complex ions. Common anions that form strong complexes with thorium include fluoride, chloride, nitrate, phosphate and sulfate. At pH values above 3, thorium undergoes hydrolysis in aqueous solutions. During the sedimentary cycle, thorium usually becomes separated from uranium because the uranium tends to mobilize in its U(VI) oxidation state until encountering a reducing environment to become immobilized U(IV). Thorium does not undergo a comparable oxidation state change.

Solid Phase and Solution Equilibria

Figure 3-24 relates the activity of Th^{4+} to pH under an assumed weathering environment in equilibrium with various thorium solid phases. The thermodynamic data for $ThO_2(s)$ were selected from Baes and Mesmer (1976). The data for the other compounds were selected from Sillen and Martell (1964). Under the assumptions outlined in Figure 3-24, all thorium compounds except ThF_4 can be arranged in an increasing order of stability throughout the pH range as follows: $Th(HPO_4)_2$, $Th_3(PO_4)_4$, $Th(OH)_4$, and ThO_2. ThF_4 would be least stable in a pH of approximately >7 and most stable approximately pH <4.

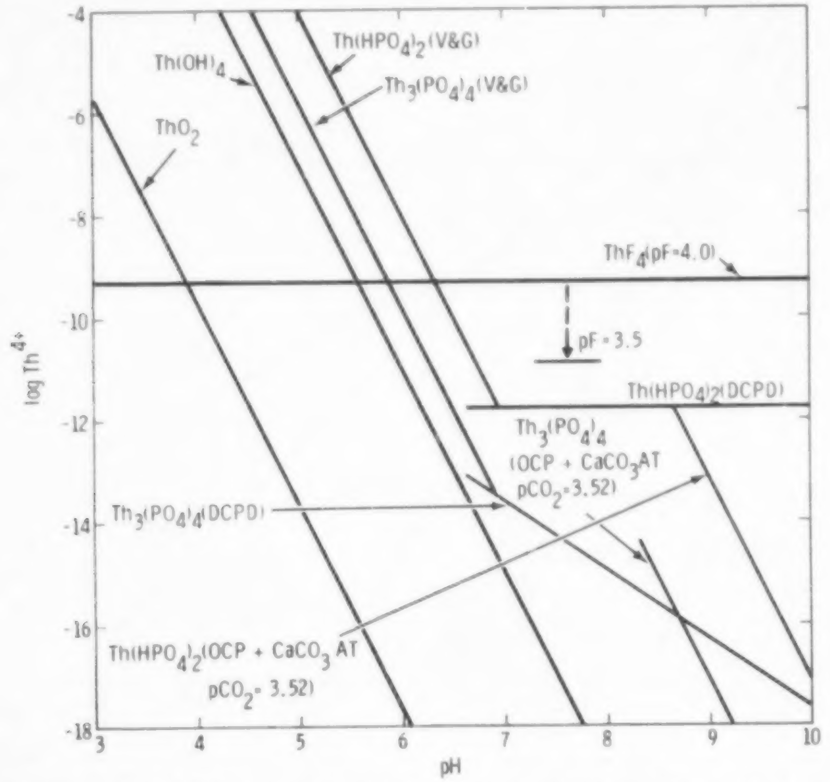

Figure 3-24. The relative stability of various thorium solids in equilibrium with Variscite and Gibbsite (V & G) Dicalcium Phosphate Dihydrate (DCPD) and Octacalcium Phosphate (OCP)

The relative activity of solution species of thorium in equilibrium with $ThO_2(s)$ at assumed activities of various ions is plotted in Figure 3-25. The thermodynamic data for all the hydrolysis species except $Th(OH)_5^-$ were obtained from Baes and Mesmer (1976). The data for all the other species and $Th(OH)_5^-$

were obtained from Sillen and Martell (1964). In general, the total concentration of thorium in solution decreases with an increase of pH from zero to 5. Above 5, pH does not affect thorium concentration in solution due to the formation of $Th(OH)_4^\circ$. The activity of all positively charged species decreases with an increase in pH, while the activity of the negatively charged species increases with the increase in pH. Under the conditions assumed for Figure 3-25, the total activity of thorium in solution would be expected to be approximately $10^{-9.6}$ moles/liter above pH 5.

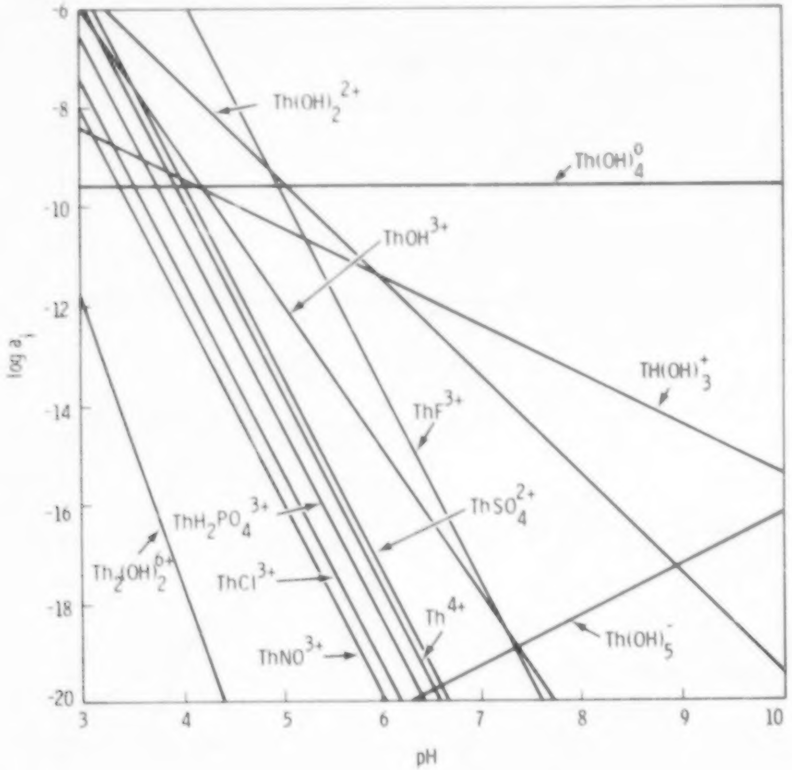

Figure 3-25. Activity of various thorium species in soil in equilibrium with $ThO_2(s)$, $pCl^- = pNO_3^- = pSO_4^{2-} = 3.0$, $pF^- = 4.5$ and $pH_2PO_4^- = 5.0$.

In addition to OH^-, thorium forms various complexes with SO_4^{2-}, PO_4^{3-}, Cl^-, NO_3^-, and F^-. Various anions in increasing order of their importance to forming complexes are: NO_3^-, Cl^-, $H_2PO_4^-$, SO_4^{2-}, and F^-. Figure 3-25 shows that thorium exists as Th^{4+} only in very acidic solutions (pH < 3). Above pH 3, Th^{4+} hydrolyzes very rapidly and it does not contribute significantly to the total thorium concentration. Under the conditions assumed for Figure 3-25, ThF^{3+} would be a dominant solution species at pH < 5, and $Th(OH)_4^o$ would be a dominant solution species at pH > 5. If fluoride ion is absent from the solution, or its concentration is extremely low, $Th(OH)_2^{2+}$ would mainly control the thorium concentration in solution at pH < 5.

Experimental Adsorption Results

Schulz (1965) found the thorium in soils to be strongly adsorbed by clay particles or present as insoluble oxides and hydroxides. Rubtsov (1966, 1972) found thorium to associate with the fine-grained particles during soil weathering. Katsurayama (1968) determined the distribution coefficient of thorium but data are not presented in the available abstract.

Nishiwaki et al. (1972) spiked seawater and seawater distilled water mixtures with Th^{+4} and measured the adsorption on a medium sand, very fine sand and silt-clay. Twenty grams of soil were contacted with 4 liters of spiked water and mixed until equilibrium was reached. The Kd for thorium increased as the particle size of the soil decreased. Chlorosity of the water did not appear to consistently affect the thorium Kd for the fine sand or silt-clay. The Kd for the medium sand increased as the chlorosity of the water decreased. The chlorosity effect was compounded by a variable pH of the various salt solutions, so that the exact cause of the trend was not determinable. Kd values for the medium sand, very fine sand and silt-clay were 40 to 130, 310 to 470, and 2700 to 10,000 ml/g, respectively.

Rancon (1973) measured the thorium Kd for a soil developed on a schist consisting of quartz and clay with no calcite or organic matter, for a mixed quartz-clay-calcite-organic matter soil and for illite with 100 mg Th/l versus solution pH. For the quartz-clay soil, at pH 6 the Kd was 5×10^5 ml/g, at pH 4 the Kd was about 1×10^3 ml/g and at pH 2 the Kd was about 5 ml/g. The mixed quartz-clay-calcite-organic matter soil could not be lowered in pH without removal of soil calcite, but above pH 8, the thorium Kd dropped from 10^6 ml/g to 100 ml/g at pH 10. Dissolution of humic acids in the soil probably resulted in thorium complexation and a decreased Kd with rising pH. Illite behaved similarly to the quartz-clay soil, but the thorium Kd at pH 1 was about 500 ml/g and about 1×10^5 ml/g at pH 6.5. For soils without calcite or organic material, the thorium Kd decreased as the thorium concentration in solution initially increased. Calcareous soils neutralized even high strength thorium solutions to precipitate $Th(OH)_4$. The quartz-clay soil and illite, for example, gave thorium Kd values of 8 ml/g and 120 ml/g, respectively, in a 1 g Th/l solution, and 60 ml/g and 1000 ml/g, respectively, in a 0.1 g Th/l solution. The drop in thorium Kd was caused by saturation of available exchange sites as a result of increased thorium concentration. There was evidence for the concentration dependence of the thorium Kd down to 1 mg Th/l in the initial contacting solution. In general, three types of soil-thorium adsorption reactions were found: 1) $Th(OH)_4$ precipitation as a result of soil calcite buffering, 2) strong adsorption on clay-containing soils and dilute thorium (<1 g/l) solutions at a pH above 2, and 3) strong adsorption on organic-containing soils at the neutral to acid pH range, but diminishing adsorption into the alkaline pH range.

Bondietti (1974) studied the adsorption of hydrolyzed thorium from waters at pH 6.5 by calcium saturated reference clays (montmorillonite and kaolinite) and calcium humate and found 95% and 99.9+% adsorption, respectively. Desorption studies utilizing calcium citrate removed 10 to 30% of the thorium from the clays but only 1% from the humate. Stronger complexers (DTPA and EDTA) removed 20 to 30% of the thorium from the humate. A mixed organic-hydroxy complex was proposed for the reaction of thorium with humic substances.

Migration Results

Field Studies--

The thorium content of groundwater was reported by Dementyev and Syromyatnikov (1965) to be highest in low salinity, low hardness, low pH, high organic content groundwaters. These characteristics suggest transport of thorium as colloidal suspensions and anionic complexes involving soil acids.

From a fresh granodiorite containing 9.3 ppm thorium and 2.5 ppm uranium, the first stages of weathering resulted in apparent removal of 25% of the thorium and 60% of the uranium (Hansen and Huntington, 1969). An acid leach of the fresh rock removed 90% of the thorium and 60% of the uranium indicating that most of the thorium and uranium are in acid soluble or interstitial materials. After an initial drop in concentration, the total uranium and thorium content of the weathered rock increases by at least a factor of 4 in the uppermost weathered material. Leaching studies showed that thorium was associated with clays formed during weathering and with accessory minerals such as zircon.

Hansen (1970) reported that when freed from minerals by weathering, thorium was leached comparatively slowly. From a fresh granodiorite containing 9.3 ppm thorium, the first stages of weathering resulted in apparent removal of 25% of the thorium. An acid leach of the fresh rock removed 90% of the thorium indicating that most of the thorium was in acid soluble or interstitial materials. The thorium content of the weathered rock increased by a factor of 4 due mostly to association with the clays formed during weathering.

Laboratory Studies--

Desai and Ganguly (1970) showed humic acids from a coastal marine sediment solubilized 100% of the thorium added to an ammonia solution (2.5N). Thorium in this solution without humic acid was observed to predominantly precipitate (95%). The humic acid-thorium complex was noncationic. In an identical experiment, fulvic acid extract was shown to solubilize 59% of thorium added to an ammonia solution. Again, the solubilized organic-thorium fraction was noncationic.

Summary

Under alkaline conditions, $Th(OH)_4$ and ThO_2 maintain low activities in soil solutions (Figures 3-24 and 3-25) and these compounds could form and govern thorium concentration. Thorium hydrolyzes readily even in moderately acidic environments (Figure 3-25) so that Th^{4+} would be present only in very acidic solutions. Laboratory studies also show that thorium tends to precipitate as thorium hydroxide and hydrated thorium oxide in soils (Schulz, 1965; Rancon, 1973).

An increase in thorium content with increase in $CaCO_3$, phosphate and humus content of soils and sediments has been reported (Kuznetsov et al., 1968; Pashneva et al., 1965; Menzel, 1968; Yakobenchuck, 1968; Hansen and Huntington, 1969; Pokidin et al., 1972). However, Tyuryukanova and Kalugina (1971) reported low thorium concentrations in high humus soils (peats and forest podzols) compared with alluvial soils. Thorium adsorption increases with increase in pH (Rancon, 1973) and decrease in soil particle size (Hansen and Huntington, 1969; Hansen, 1970; Nishiwaki et al., 1972; Rubtsov, 1966, 1972; Bondietti, 1974). Strong humic and fulvic acid complexes with thorium occur in the neutral to acidic range (Rancon, 1973; Bondietti, 1974) which are noncationic (Desai and Ganguly, 1970) and mobile. It has been reported also that thorium migrates primarily in the colloidal form (polymeric) in the natural environment (Baranov et al., 1956; Lazarev et al., 1961; Kimura et al., 1968).

References

Adams, J. A. S., J. K. Osmond, and J. J. W. Rogers. 1959. The Geochemistry of Thorium and Uranium. IN: Physics and Chemistry of the Earth. 3. L. H. Ahrens, F. Press, K. Rankama, and S. K. Runcorn (eds.), pp. 298-348.

Adams, J. A. S. and K. A. Richardson. 1960. Thorium, Uranium, and Zirconium Concentrations in Bauxite. Econ. Geol. 55:1653.

Adams, J. A. S. and C. E. Weaver. 1958. Thorium-to-Uranium Ratios as Indicators of Sedimentary Processes -- An Example of Geochemical Facies. Bull. Am. Assoc. Petrol. Geol. 42:387.

Ahrens, L. H. 1952. The Use of Ionization Potentials. Part I. Ionic Radii of the Elements. Geochim. et Cosmochim. Acta. 2:155.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Baranov, V. I., A. B. Ronov, and K. G. Kinashova. 1956. On Geochemistry of Dispersed Thorium and Uranium in Clays and Carbonate Rocks of Russian Platform. Geokhimiya No. 3:3-8.

Billings, G. K. 1962. A Geochemical Investigation of the Valley Spring Gneiss and Packsaddle Schist, Llano Uplift, Texas. Texas J. Sci. 9:328.

Bondietti, E. A. 1974. Adsorption of Pu(IV) and Th(IV) by Soil Colloids. Agronomy Abstracts.

Dementyev, V. S. and N. G. Syromyatnikov. 1965. Mode of Occurrence of Thorium Isotopes in Ground Waters. Geokhimiya. No. 2:211-218.

Desai, M. V. M. and A. K. Ganguly. 1970. Interaction of Trace Elements with Organic Constituents in the Marine Environment. BARC-488, p. 102.

Hansen, R. O. 1970. Radioactivity of a California Terrace Soil. Soil Science. 110:31-36.

Hansen, R. O. and G. L. Huntington. 1969. Thorium Movements in Morainal Soils of the High Sierra, California. Soil Science. 108:257-265.

Heier, K. S. and J. L. Carter. 1964. Uranium, Thorium, and Potassium Contents in Basic Rocks and Their Bearing on the Nature of the Upper Mantle. IN: J.A.S. Adams and W. M. Lowder (eds.). The Natural Radiation Environment, p. 75.

Heier, K. S. and J. J. W. Rogers. 1963. Radiometric Determination of Thorium, Uranium, and Potassium in Basalts and in Two Magmatic Differentiation Series. Geochim. et. Cosmochim. Acta. 27:137.

Holland, H. D. and J. L. Kulp. 1954. The Mechanism of Removal of Thorium and Radium from the Oceans. Geochim. et Cosmochim. Acta. 5:214-224.

Katsurayama, K. 1968. Accumulation of Radioactivity in Rice Fields. Annu. Rep. Res. Reactor Inst. Kyoto University. 1:293-97.

Kimura, Y., H. Morishuma, T. Koga, H. Kawai and Y. Honda. 1968. Studies on the Behavior and Distribution of Radioactive Substances in Coastal and Estuarine Waters. Kinki Daigaku Genshiryaku Kenkyusho Nonpo. 7:21-31 (in Japanese).

Kuznetsov, Y. V., Z. N. Simonyak, A. P. Lisitsyn, and M. S. Frenklikh. 1968. Thorium Isotopes (^{230}Th, ^{232}Th) in the Surface Layer of the Indian Ocean Sediments. Geochem. Int. 5:169-77.

Lazarev, K. F., D. S. Nikolaev, and S. M. Grashchenko. 1961. Concentration of Thorium Isotopes in Sea Water. Radiokhimiya. 3:623-35 (in Russian).

Menzel, R. G. 1968. Uranium, Radium, and Thorium Content in Phosphate Rocks and Their Possible Radiation Hazard. J. Agr. Food Chem. 16:231-34.

Murray, E. G. and J. A. S. Adams. 1958. Amount and Distribution of Thorium, Uranium, and Potassium in Sandstones. Geochim. et. Cosmochim. Acta. 13:260.

Nishiwaki, Y., Y. Honda, Y. Kimura, H. Morishima, T. Koga, Y. Miyaguchi, and H. Kawai. 1972. Behavior and Distribution of Radioactive Substances in Coastal and Estuarine Waters. IN: Radioactive Contamination of the Marine Environment. IAEA-SM-158/11, pp. 177-193.

Pashneva, G. E., T. P. Slavnina, and V. V. Serebrennikov. 1965. Rare Earth and Thorium Content in Soils of Tomsk Region. Izv. Sibirsk. Otd. Akad. Nauk SSSR, No. 4 Ser. Biol.-Med. Nauk. No. 1:48-52 (in Russian).

Pliler, R. 1956. The Distribution of Thorium and Uranium in Sedimentary Rocks and the Oxygen Content of the Precambrian Atmosphere. Thesis. Rice Institute.

Pokidin, V. K., Y. V. Kuznetov, E. A. Prozorovich, and F. A. Asadullaeva. 1972. Radioactivity and Rate of Sediment Formation in the Caspian Sea. Geokhimiya. No. 7:834-43 (in Russian).

Rancon, D. 1973. The Behavior in Underground Environments of Uranium and Thorium Discharged by the Nuclear Industry. IN: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/55, pp. 333-346 (in French).

Rogers, J. J. W. 1964. Statistical Test of the Homogeneity of the Radioactive Components of Granite Rocks. IN: J.A.S. Adams and W. M. Lowder (eds.), The Natural Radiation Environment, p. 51.

Rogers, J. J. W. and J. A. S. Adams. 1974. Thorium Solubilities in Water. Handbook of Geochemistry, K. H. Wedepohl, Ed., Vol. II-4, p. 90-H-1, Springer-Verlag, New York.

Rubtsov, D. M. 1966. Distribution of Thorium in Various Soils. Pochvovedenie. No. 3:55-67 (in Russian).

Rubtsov, D. M. 1972. Thorium and Radium Content in the Silt Fraction of the Podzolic Mountain Soils of Thin Forests. Radioekologicheskie Issledavaniya Prirodnykh Biogeotsenozakh. IN: Verkhovskaya (ed.) Izdatel'stov Nauka, pp. 42-53.

Ryabchikov, D. I. and E. K. Golbraikh. 1969. Analytical Chemistry of Thorium. Translated by A. Aladjem. Ann Arbor-Humphrey Science Publishers.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-24.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Tyuryukanova, E. B. and V. A. Kalugina. 1971. The Behavior of Thorium in Soils. Soviet Journal of Ecology. 2:467-469.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau, Inc.

Yakobenchuk, V. F. 1968. Radioactivity and Chemical Properties of Sod-Podzolic Soils in the Ukrainian Western Polesie. Visn. Sil's' Kogosped. Nauki. 11:45-50 (in Ukranian).

TRITIUM

Natural Soil and Rock Distributions

Natural tritium concentrations vary geographically from about 10 T.U. for northern and southern midlatitude precipitation to 1 T.U. for equatorial precipitation. The background tritium content of deep ocean and groundwater is essentially zero (Fairbridge, 1972). Hence, the tritium content of rocks, minerals and deeper sediments also is nearly zero unless contacted by tritium-contaminated groundwater.

Brief Chemistry

Tritium (^3H or T) is an isotope of hydrogen with a half-life of 12.26 years. Tritium occurs naturally in the upper atmosphere, chiefly by the interaction of fast neutrons with nitrogen (Kaufman and Libby, 1954). The amount of natural tritium is about one part in 10^{17} parts of normal hydrogen (^1H) (Cotton and Wilkinson, 1962).

It was a fairly recent discovery that tritium also is a product of uranium fission (Albenesius, 1959; Albenesius and Ondrejcin, 1960). Several years prior to the identification of tritium as a uranium fission product, the Environmental Monitoring Group at Savannah River plant recognized tritium as occurring in Purex separations process wastes, and was using it as a groundwater tracer (Horton and Ross, 1960). Tritium yields of 3.8 to 20.3 curies/ton uranium were obtained for exposures between 300 and 1600 megawatt-days/ton uranium.

Tritium oxidizes rapidly to HTO, existing essentially as water, and its distribution in ground and surface waters is controlled by the operation of the hydrological cycle. Tritium is measured in tritium units, T.U., where $T.U. = T/10^{18}H$, or expressed as picocuries/liter. Natural background levels have risen since weapons testing of nuclear devices from 1 to 10 T.U. to several hundred T.U. up to the 1963 atmospheric detonation moratorium. Most of the tritium added to the hydrological cycle by fusion devices was due to residual tritium ($\sim 6.7 \times 10^6$ Ci ^3H/megaton fusion device, Stead, 1963).

Solid Phase and Solution Equilibria

Tritium (H^3) is a radioactive isotope of hydrogen. Thus, tritium behavior in soils would be expected either to be similar to hydrogen or to exist as an ion, gas and liquid (tritiated water). Except for the slight differences in vapor pressure, tritiated water behaves the same as ordinary water (Jacobs, 1974). Although no discrete solid phases of tritium are expected in soils, it could associate itself with soil organic components containing hydrogen or with some soil minerals as mobile water, water of hydration, or as part of structural hydroxyl groups (Jacobs, 1974; Stewart, 1967).

Tritium rapidly travels at about the same velocity as the soil water or groundwater in the form of HTO. Some replacement of nontritiated water on clays and other hydrated soil constituents occurs, but the reaction is of marginal value as far as tritium retention is concerned. Tritium can move in a vapor phase through the soil under certain conditions as well.

Experimental Adsorption Results

Tritium ultimately exists in the soil as a tritiated water molecule. Theoretically, tritium ions are capable of exchanging for hydrogen and other ions on soil. However, the tritium is usually in an aqueous solution before contacting soils, so that isotopic exchange and replacement of hydroxyl water molecules is the most common mechanism of tritium removal. Little quantitative work on tritium distribution has been reported. Rabinowitz et al. (1973) have used an electrodialysis technique to speed up tritium hydroxyl exchange in clays. They reported that tritium hydroxyl exchange was proportional to cation exchange capacity of the clays used in the study: illite, 35 meq/100 g and 93 pCi ^3H/ml; kaolinite No. 4, 10 meq/100 g and 36 pCi ^3H/ml; kaolinite No. 9, 2 meq/100 g and 12 pCi ^3H/ml. Most of the field studies indicated that tritium distribution coefficients were very low because tritium migration velocities were essentially the same as those of the accompanying groundwater (Brown and Haney, 1964; Brown, 1967).

Migration Results

Field Studies--

Haney, Brown and Reisenauer (1962) and Brown and Haney (1964) estimated by studying the rate and direction of groundwater flow that movement of tritium disposed to the ground at the Hanford Purex Plant would require 6 or 7 years travel time to the Columbia River, approximately 17 miles from the Purex Plant. The half-life of tritium allowed about 70% of the total tritium discharged to reach the river. The tritium content of Columbia River water was not expected to rise over 50% higher than the present background because of tritium dispersion during travel and the large dilution represented by the Columbia River (80,000 to 200,000 ft^3/sec).

Brown (1967) reviewed the hydrology and geology of the Hanford area, and showed the 1966 limits of the areas defined by 3000 pCi/cm^3 and 10 pCi/cm^3 of tritium based on well water analytical results. The 10 $pCi\,^3H/cm^3$ area was 3 km from the Columbia River in 1966. The concentration of tritium added at the Purex Plant disposal sites was 10,000 $pCi\,^3H/cm^3$. Tritium moved at essentially the same rate as the groundwater.

Kline and Jordan (1968) reported a field experiment on a clay Puerto Rican soil where 1 liter of 20 mCi/l tritiated water was applied to a plot with about 1 m^2 area, and sampled via a lysimeter installed horizontally, without disturbing the plot surface soil, 18 cm below the soil surface. The sampling program lasted 210 days during which time 137 cm of rain fell on the plot. Runoff surface water was collected as well. The soil remained saturated, or close to saturation for the sampling period. Most of the tritium passed through the profile as a peak or front 16 days after application, and declined in concentration exponentially during the remainder of the experiment. The surface runoff peaked in 2.9 days, with another change in decline of specific activity at 35.6 days. Because of the loss rate curve of tritium in the free soil water, the authors suggested that tritium movement through soils must be modified to allow for the existence in clay soils of isolated compartments of immobile water that does not have free interchange with the more rapidly moving water.

Jordan et al. (1971) monitored tritium movement through a soil near Argonne, Illinois. They concluded from the results that a pulse of tritium moves downward at a rate determined by precipitation entering the top of the soil column. The tritium peak broadens and flattens from diffusion and will become immobilized if the upper soil layers dry out. Loss of tritium occurred both by evapotranspiration and deep drainage. Deviation of the field results from a model of tritiated water movement proposed by Sasscer et al. (1971) was explained as due to parameters that were difficult to quantify such as root holes and hydroxyl exchanges.

Ehhalt (1973) pointed out that tritiated molecular hydrogen in the atmosphere was oxidized by soil microorganisms. He also estimated from the tritium content of H_2 of 2×10^6 T.U., steady since 1962, that the HT input rate was about 5.4 T atoms/cm^2 sec into the soil from the action of soil microorganisms.

Purtymun (1973) investigated the underground movement of tritium from solid waste storage shafts in rhyolite tuff at Los Alamos. Levels of 100 pCi ^{3}H/ml had moved a distance of 105 ft in 4 years. Core samples of tuff were collected, water distilled from them and tritium in the water determined. Asphalt coatings on containers and shaft walls was suggested to control tritium migration from the shafts.

In contrast, Wheeler and Warren (1975) reported that a later comparison between asphalted and nonasphalted shafts showed that the asphalt containment techniques used were ineffective in slowing tritium migration from the shafts. Double containment and complete encapsulation of the 210-liter disposal drums in roofing asphalt was suggested to slow tritium movement from the storage shafts.

Laboratory Studies--

Because soil water and groundwater systems are similar, it would be expected that tritium oxide would move through these systems at essentially the same rate as light water. However, in comparing chloride ions and tritium breakthrough curves for various soil types, the tritium curve lags behind that for chloride ions in soils containing clays and silt (Kaufman and Orlob, 1955). This behavior was reported as caused by the tritiated water molecule entering the clays and replacing nontritiated water adsorbed on clay surfaces or interlayers.

Haney (1963, 1964) reported a laboratory study where actual groundwater containing complexed ^{106}Ru and tritium was passed through several Hanford project soils. In silty soils, the ruthenium breakthrough curve was slightly behind that for tritium, but in sandy soil columns, the breakthrough curves were essentially identical. Several retention mechanisms of tritium on clays are possible. For example: 1) exchange of tritium ions for hydrogen ions in exchange positions, 2) tritiated water molecules exchanged for hydroxyl water or water of crystallization, 3) exchange of tritium ions for exchangeable cations other than hydrogen, and 4) replacement of aluminum in lattice sites by tritium, with the aluminum ions moving into exchangeable cation positions. In the last case, the tritium may be more or less "fixed" in its octahedral position. This "fixation" has been considered to be minimal by some investigations (Higgins, 1959; Halevy, 1964; Corey and Horton, 1968; Teller et al., 1968).

It has been hypothesized by others (Corey and Fenimore, 1968) that the chloride ions are repelled from negatively charged soil particles into the central region of the soil pore where groundwater velocity is greatest (anion exclusion). This would be most effective in high cation exchange capacity soils which do not retain anions. Also, Corey and Fenimore (1968) showed that chloride ions lag far behind tritium in acid kaolinitic soil due to anion exchange of the chloride ions.

Corey and Horton (1968) reported no appreciable tritium "fixation" upon investigation of the movement of tritiated and deuterated water through acidic, kaolinitic soil. The work of other investigators, however, indicates that hydrogen isotopes may be selectively fixed (Rosenqvist, 1963; Koranda, 1965; Clayton et al., 1966; Savin, 1967; Stewart, 1967). The work of Rabinowitz (1969) and Rabinowitz et al. (1973) with forced exchange of tritiated water on clays also supports the view that part of the tritium can be "fixed" on clays. The isotopic exchange and fixation was forced with a mild form of electrodialysis (2 V/cm) resulting in an increase in the reaction rate of about five times the rate without electrodialysis. Aluminum and other basing cations were determined after each experiment. The presence of exchangeable Al^{+3} correlated with tritium loss from the water resulting from tritium "fixation". A mass balance on the tritium also was determined for each experiment. The analytical data for tritium facilitated the differentiation of isotopic exchange and the "fixation" of tritium by kaolinite and illite.

Summary

Tritium substitutes readily for the hydrogen in water and thus becomes a part of the hydrological cycle (Jacobs, 1974). Migration of tritium through the groundwater takes place at the same velocity as the groundwater through sandy soils (Haney 1963, 1964; Haney et al., 1962; Brown and Haney, 1964; Brown, 1967). Some investigators have reported the selective fixation of tritiated water on clays and other hydrated minerals (Rosenqvist, 1963; Koranda, 1965; Clayton et al., 1966; Savin, 1967; Stewart, 1967; Rabinowitz, 1969; Rabinowitz et al., 1973) while other investigators have considered tritium fixation to be minimal (Higgins, 1959; Halevy, 1964; Corey and Horton, 1968; Teller et al., 1968). However, all of the field studies have indicated that tritium movement is synonomous with water movement (Brown, 1967).

References

Albenesius, E. L. 1959. Tritium as a Product of Fission. Physics Review Letters. 3:274.

Albenesius, E. L. and R. S. Ondrejcin. 1960. Nuclear Fission Produces Tritium. Nucleonics. 18:100.

Brown, D. J. 1967. Migration Characteristics of Radionuclides Through Sediments Underlying the Hanford Reservation. ISO-SA-32.

Brown, D. J. and W. A. Haney. 1964. Chemical Effluents Technology Waste Disposal Investigations July-December, 1973 - The Movements of Contaminated Ground Water from the 200 Areas to the Columbia River. HW-80909.

Clayton, R. N., I. Friedman, D. L. Graaf, T. K. Mayeda, W. F. Meents and N. F. Shimp. 1966. The Origin of Saline Formation Waters. I. Isotopic Composition. J. Geophys. Res., 71, 3869-3882.

Corey, J. C. and J. W. Fenimore. 1968. Tracing Groundwater with Chloride Ions and Tritium Through Acid Kaolinitic Soil. Int. J. Appl. Rad. Isotopes. 19:741-746.

Corey, J. C. and J. H. Horton. 1968. Movement of Water Tagged with ^{2}H, ^{3}H and ^{18}O Through Acidic Kaolinitic Soil. Soil Sci. Soc. Am., Proc. 32:471-475.

Cotton, F. A. and G. Wilkinson. 1962. Advanced Inorganic Chemistry. Interscience Publishers.

Ehhalt, D. H. 1973. On the Uptake of Tritium by Soil Water and Ground Water. Water Resources Research. 9:1073-1074.

Fairbridge, R. W. (ed.). 1972. The Encyclopedia of Geochemistry and Environmental Sciences. Van Nostrand Reinhold Company.

Halevy, E. 1964. The Exchangeability of Hydroxyl Groups in Kaolinite. Geochim. et Cosmochim. Acta. 28:1139-1145.

Haney, W. A. 1963. Fission Product Tritium in Fuel Reprocessing Wastes. HW-SA-3303.

Haney, W. A. 1964. Consequences of Activity Release. Nuclear Safety. 5:399-403.

Haney, W. A., D. J. Brown, and A. E. Reisenauer. 1962. Fission Product Tritium in Separations Wastes and in the Ground-Water. HW-74536.

Higgins, G. H. 1959. Evaluation of the Ground-Water Contamination Hazard from Underground Nuclear Explosions. J. Geophys. Res. 64:1509-1520.

Horton, J. H. and D. I. Ross. 1960. Use of Tritium from Spent Uranium Fuel Elements as a Ground-Water Tracer. Soil Science. 90:267-271.

Jacobs, D. C. 1974. Impacts in Groundwater of Effluents Arising in the Nuclear Industry. NP-20456, pp. vp., Paper 16.

Jordan, C. F., J. R. Kline, and D. S. Sasscer. 1971. Tritium Movement in an Old-Field Ecosystem Determined Experimentally. IN: Radionuclides in Ecosystems. CONF-710501-P1, pp. 199-203.

Kaufman, S. and W. F. Libby. 1954. The Natural Distribution of Tritium. Phys. Rev. 93:1337.

Kaufman, W. J. and G. T. Orlob. 1955. Measuring Ground Water Movement with Radioactive and Chemical Tracers. Paper presented at the Annual Meeting of the California Section of AWWA, Sacramento.

Kline, J. R. and C. F. Jordan. 1968. Tritium Movement in Soil of Tropical Rain Forest. Science. 160:550-551.

Koranda, J. J. 1965. Preliminary Studies of the Persistence of Tritium and ^{14}C in the Pacific Proving Ground. Health Phys., 11, 1445-1457.

Purtymun, W. D. 1973. Underground Movement of Tritium from Solid-Waste Storage Shafts. LA-5286-MS.

Rabinowitz, D. D. 1969. Forced Exchange of Tritiated Water with Natural Clay. MS Thesis, N. Mex. Inst. of Min. and Tech., Socorro, NM.

Rabinowitz, D. D., C. R. Holmes and G. W. Gross. 1973. Forced Exchange of Tritiated Water with Clays. IN: Tritium, Messenger Graphics Pub., Phoenix and Las Vegas, 471-485.

Rosenqvist, I. T. 1963. Studies in Position and Mobility of the H Atoms in Hydrous Micas. IN: Clays and Clay Minerals, Monograph No. 13, p. 11-135, Macmillan Co., NY.

Sasscer, D. S., C. F. Jordan, and J. R. Kline. 1971. Mathematical Model of Tritiated and Stable Water Movement in an Old-Field Ecosystem. IN: Radionuclides in Ecosystems. CONF-710501-P1, pp. 915-923.

Savin, A. M. 1967. Oxygen and Hydrogen Isotope Ratios in Sedimentary Rocks and Minerals. PhD Dissertation, Calif. Inst. of Tech. Pasadena, CA.

Stead, F. W. 1963. Tritium Distribution in Ground Water Around Large Underground Fusion Explosions. Science. 142:1163-1165.

Stewart, G. L. 1967. Fractionation of Tritium and Deuterium in Soil Water. IN: Isotope Techniques in the Hydrologic Cycle, Geophys. Monograph No. 11, 159-168.

Teller, E., W. K. Talley and G. H. Higgins. 1968. The Constructive Uses of Nuclear Explosives. McGraw-Hill, New York.

Wheeler, M. L. and J. L. Warren. 1975. Tritium Containment After Burial of Contaminated Solid Waste. Trans. Am. Nucl. Soc. 22:741.

URANIUM

Natural Soil and Rock Distributions

The range in abundance of uranium in natural rocks is given in Table 3-96. Vinogradov (1959) reported 1 ppm uranium as the average content of uranium in soils. The oxidation of organic matter in black shales tends to precipitate U(IV). Consequently, the black shales usually contain more uranium than red, green or gray shales.

Brief Chemistry

There are 14 known isotopes of uranium from ^{227}U to ^{240}U and one uranium isomer (^{235}U) (Fairbridge, 1972). The half-lives of the uranium isotopes vary from a few minutes to over 4 billion years. Only three of the isotopes occur naturally, and two of these (^{235}U and ^{238}U) are parents of series that end in lead isotopes. The nuclear data on the three natural uranium isotopes are given in Table 3-97. The uranium isotopes of interest in waste disposal are given in Table 3-98. The common oxidation states of uranium are U(III), U(IV), U(V) and U(VI) (Udaltsova, 1963). U(III) is easily oxidized in air to U(IV).

TABLE 3-96. ABUNDANCES OF URANIUM IN NATURAL MATERIALS (ADAMS ET AL., 1959; CLARK ET AL., 1966)

Material	U Concentration Range, ppm	
Igneous Rocks		
Dunites and Peridotites	0.001-0.8	
Gabbro and Diabase	0.3-3.4	Median 0.5
Intermediate (diorite and quartz diorite)	0.1-11.0	Median 1.7
Sialic (granite, syenite, monaozite)	0.15-21.0	Median 3.9
Sedimentary Rocks		
Black shales	3.0-25.0	Median 8.0
Red, gray and green shales	1.2-12.0	Median 3.2
Orthoquartzite	0.2-0.6	Median 0.45
Limestone and dolomite	0.1-9.0	Median 2.2
Bentonite	1.0-21.0	Median 5.0
Bauxite	3.0-27.0	Median 8.0
Halite	0.01-0.02	Median 0.013
Anhydrite	0.25-0.43	Median 0.37
Metamorphic Rocks		
Marble	0.11-0.24	
Slate	1.2-6.1	
Phyllite	1.0-2.7	
Schist	1.8-2.9	
Gneiss	4.5-15.0	
Amphibolite	2.6-4.1	
Granulite	3.2-7.0	

The U(IV) state is fairly stable in aqueous solutions if they are very acidic. Uranium (V) disproportionates to U(IV) and U(VI): $2UO_2^+ + 4H_3O^+ \rightarrow UO_2^{+2} + U^{+4} + 6H_2O$ (Udaltsova, 1963). U(VI), as UO_2^{+2} (Uranyl) at $pH \leq 2.5$, is the most

TABLE 3-97. NUCLEAR PROPERTIES OF NATURAL URANIUM ISOTOPES (FAIRBRIDGE, 1972)

Isotopes	% Abundance	Half-Life, yr	Decay Series Parent
^{234}U	0.0056	2.48×10^5	-
^{235}U	0.72	7.13×10^8	4N + 3
^{238}U	99.27	4.51×10^9	4N + 2

TABLE 3-98. URANIUM RADIONUCLIDE DATA (WEAST, 1976)

Isotope	Half-Life	Decay Mode
^{232}U	73.6 years	α, SF
^{233}U	162,000 years	α
^{234}U	247,000 years	α
^{235}U	7.13×10^8 years	α, SF
^{236}U	2.39×10^7 years	α, SF
^{237}U	6.75 days	β^-
^{238}U	4.51×10^9 years	α, SF

stable state of uranium in aerated aqueous solutions (Seaborg and Katz, 1954). At higher pH values, hydrolyzed uranyl ions predominate. Approximately 103 uranium minerals have been confirmed. Uraninite (ideally UO_2) is the primary ore mineral of uranium, but other secondary minerals include carbonates, sulfates, molybdates, phosphates, vanadates, silicates and multiple oxides. Uranyl ions readily form many complexes with anions ordinarily found in soil-water environments such as carbonate, sulfate and fluoride.

Solid Phase and Solution Equilibria

The thermodynamic data for 1) UO_3, Na_2UO_4 and UO_2CO_3 were obtained from Garrels and Christ (1965), 2) $UO_2(OH)_2$, $UO_2(OH)_2H_2O$ and $Na_4UO_2(CO_3)_3$ were obtained from Sillen and Martell (1964), and 3) the remaining species reported in Figure 3-26 were obtained from Palei (1970). The relative stability of several uranium solid phases, in terms of the uranyl ion activity produced by each, is shown in Figure 3-26. Since all the compounds shown in Figure 3-26 are of U(VI), and are plotted as a function of UO_2^{2+}, their curves would not move with changes in oxidation-reduction conditions. U(IV) compounds, such as UO_2, are very soluble in an oxidizing environment and fall outside the boundary of Figure 3-26. With an increase in reducing conditions, U(IV) compounds would become more stable. At a pO_2 of >71, the UO_2 curve would fall just below the $UO_2NH_4PO_4$ curve. U(VI) compounds are stable in an oxidizing environment and U(IV) compounds are stable in a reducing environment. Consistent with the thermodynamic data is the observation that carnotite, a U(VI) mineral is found in the oxidized zones of uranium ore deposits and uraninite, a U(IV) mineral is a primary mineral in reducing ore zones.

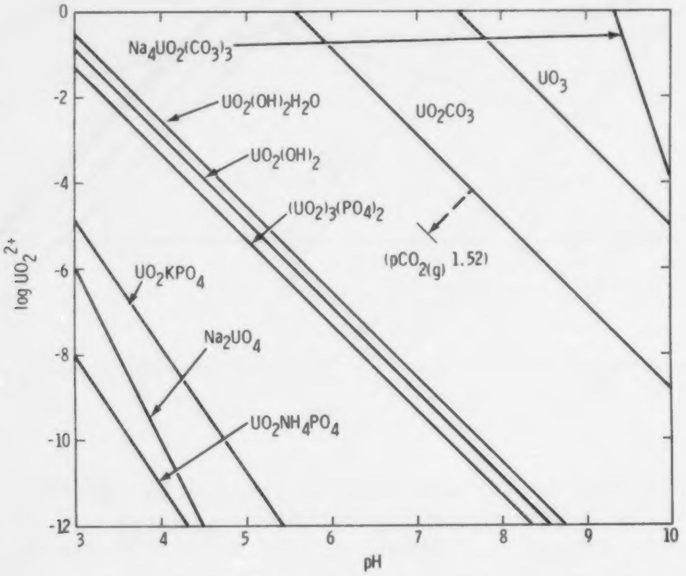

Figure 3-26. The relative stability of various uranium solids in an oxidizing soil environment [$pO_2(g)$ = 0.68 atm], $PCO_2(g)$ = 3.52 atm, pK^+ = pNa^+ = pNH_4^+ = 3.0 and phosphate levels in equilibrium with Variscite and Gibbsite.

The thermodynamic data for UO_2F^+ and $UO_2H_2PO_4^+$ were selected from Palei (1970) and selected data from Sillen and Martell (1964) were used for the remaining species in Figure 3-27. All the species except UO_2^+ shown in Figure 3-27 are of U(VI). Since equilibrium is assumed with Na_2UO_4, a U(VI) compound, a change in oxidation-reduction conditions will affect the position of the curves. In an oxidizing environment (pO_2 = 0.68 atm), the U(IV) species are very low in concentration ($\log a_i < 38$) and fall outside of the boundaries of Figure 3-27.

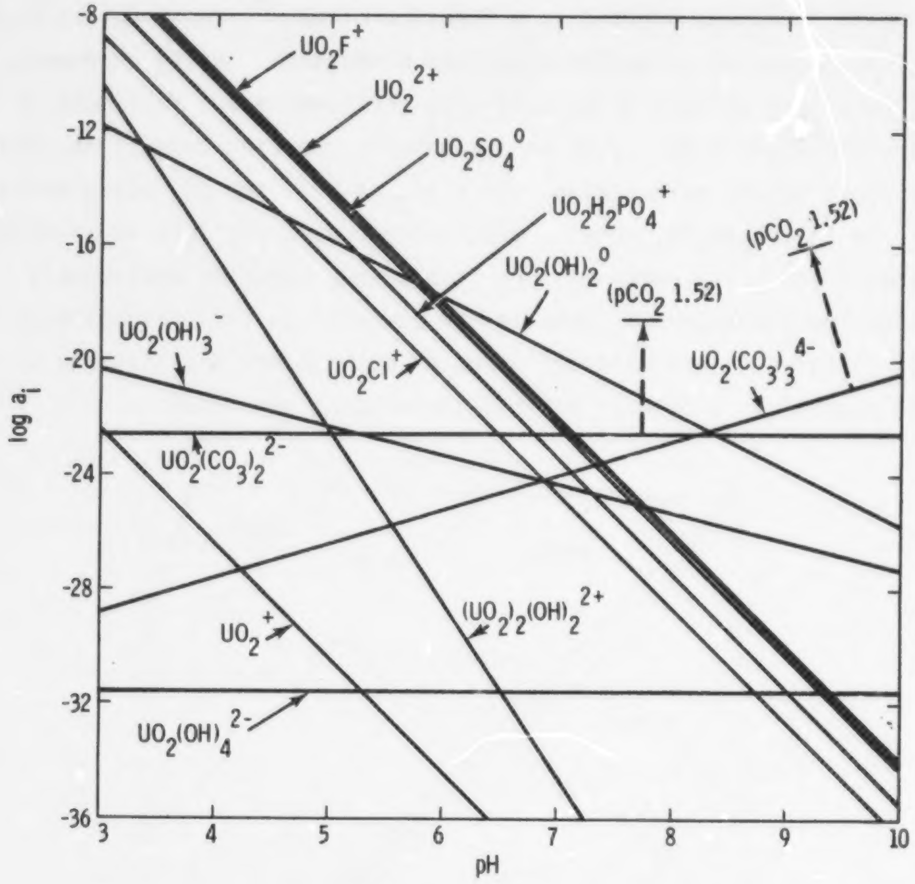

Figure 3-27. Activity of various uranium species in equilibrium with Na_2UO_4 in an oxidizing soil environment [$pO_{2(g)}$ = 0.68 atm], $pCO_{2(g)}$ = 3.52 atm, pCl^- = pSO_4^{2-} = 3.0, pF^- = 4.5 and pH_2PO_4 = 5.0.

Figure 3-27 shows that U(VI) species will control the solution concentration in an oxidizing environment. UO_2^{2+} is the predominant solution species up to a pH of approximately 6. The predominant solution species over pH ranges of from 6 to 8 and >8 are $UO_2(OH)_2^\circ$ and $UO_2(CO_3)_3^{4-}$, respectively.

Experimental Adsorption Results

Uranium adsorption studies have been performed by several investigators. Szalay (1954, 1957) showed that uranium adsorption by decomposing plant debris, peat, lignite and brown coal is quite high. He determined that humic substances in these materials were responsible for the adsorption which was described as an ion exchange-like sorption. Adsorption isotherms for the humic acid were measured.

Goldsztaub and Wey (1955) determined that 7.5 g of uranium was adsorbed from a 1% uranyl nitrate solution per 100 g of calcined montmorillonite and 2.0 g of uranium per 100 g of calcined kaolinite.

Manskaya et al. (1956) described the adsorption of uranium on fulvic acids as a function of pH. The curve of percent adsorption versus pH showed a maximum at pH 6 of about 90% uranium removal. At pH 4 and pH 7, uranium adsorption was down to 30%.

Starik et al. (1958) showed a similar adsorption curve of pH versus uranium adsorption on ferric hydroxide. The maximum of the adsorption curve was at pH 5 with about 50% uranium adsorption, and rapidly decreased above and below pH 5.

Rozhkova et al. (1959) showed similar uranium adsorption curves versus pH for lignite and humic acids. The curve maxima occurred between pH 5 and 6. Dementyev and Syromyatnikov (1968) showed that these adsorption curve maxima result because the pH 6 region is a boundary between anionic and cationic uranium forms and corresponds to: $[UO_2^{+2}] + [UO_2OH^+] \cong [UO_2(CO_3)_2^{-2}]$, an equality between cation and anion uranium forms in solution.

Horráth (1960) measured the enrichment factor for the adsorption of uranium by peat and obtained an average of 200 to 350. Although it is not possible to determine what methods or exactly what the enrichment factor means from the English translated abstract, it is assumed that the data represent a uranium Kd of 200 to 350 by weight or volume.

Kovalevskii (1967) found the uranium content of noncultivated soils in western Siberia increased with the clay content of the soils. Clay soils contained at least three times as much uranium as sands. Yakobenchuck (1968) correlated the total uranium content in Russian sodpodzilic soils from the Ukraine with other soil constituents. Uranium showed correlation with the oxidizes of silicon, iron, and aluminum suggesting coprecipitation or inclusion.

Masuda and Yamamoto (1971) studied the adsorption of uranium (1 to 100 ppm U) dissolved in water onto volcanic ash, alluvial, and sandy soils. The uranium was almost completely adsorbed on each of the soils. Uranium desorption with salt solutions was extremely difficult especially for the volcanic ash. Similar studies by Yamamoto et al. (1973) on the three soils using uranium (1 to 50 ppm U) and carbonated waters (4 to 109 ppm CO_3^{-2}) showed approximately 100% adsorption and less than 2% desorption.

Rubtsov (1972) determined the uranium content in forest podzolic mountain soils and found a relatively high level of uranium in the <1 μ particle size fraction of the podzolic A_2 horizon. In general, for the soils studied 58% of the total uranium was found in the <1 μ soil fractions. Ritchie, Hawks, and McHenry (1972) found the uranium content of sediments from the Little Tallahatchie River to increase with decreasing particle size.

Rancon (1973) studied the adsorption of uranium using four soils described as follows: 1) a river sediment containing a mixture of quartz, clay, calcite and organic matter, 2) a river peat, 3) a sediment from Cadarache containing a mixture of quartz, clay and calcite with no organic matter, and 4) a soil developed on an altered schist from near LaHague containing a mixture of quartz and clay but no calcite or organic matter. The first two soils were equilibrated with their river waters containing 10 ppm uranium and the last two soils were equilibrated with their respective groundwaters also containing 10 ppm uranium. The resulting uranium distribution coefficients are shown in Table 3-99, which also includes the Kd values on pure quartz, calcite and illite. The clay minerals in Soils 1, 3 and 4 were not identified or the soils further characterized. Rancon also examined the effects of initial uranium concentration on Kd values. Both the uranium concentration and solution pH changed as uranium was added to the solution. At 0.1 mg U/l, the pH was 7.6, for example, and at 1.0 g U/l, the pH was 3.5. Because the pH changes are a function of uranium concentration changes, the results are not easily interpreted. In addition, the Kd concept is invalid above the trace uranium concentration (∿1.0 mg U/l). Uranium adsorption data at 1 ppm versus Kd also are presented. For Soil 4, three peaks were observed: Kd 300 ml/g at about pH 5.5, Kd 2000 ml/g at pH 10 and Kd 270 ml/g at pH 12.

TABLE 3-99. URANIUM Kd VALUES (RANCON, 1973)

Soil	Kd, ml/g
1 - River Sediment (clay, $CaCO_3$, OM)	39
2 - River Peat	33
3 - Sediment (clay, $CaCO_3$)	16
4 - Altered Schist (clay)	270
Quartz	0
Calcite	7
Illite	139

Rancon believed that the adsorption maxima represented by the three peaks also represent electrokinetic potential maxima. Quartz was characterized as inert, calcite was a poor uranium adsorber and clays were the best adsorbers of uranium from solution. Acid, organic-rich soils show much higher uranium Kd values than the alkaline peat (Soil 2) of this study.

Migration Results

Field Studies--

A study of granitic rock weathering by Harriss and Adams (1966) included autoradiographs of fresh and weathered samples of several granitic rocks. There was a definite increase in the density of concentrated radioactive materials with weathering. However, analyses indicated a small loss for uranium. The increased density, therefore, must be due to losses of other materials (alkalies and alkaline earths) during weathering. From a fresh granodiorite containing 2.5 ppm uranium, the initial weathering resulted in losses of 60% of the uranium. An acid leach of fresh rock also removed 60% of the uranium indicating that most of the uranium was in acid soluble or interstitial materials. After an initial drop in concentration, the total uranium content of the weathered rock increased by at least a factor of 4 in the uppermost material.

Laboratory Studies--

Schulz (1965) suggested that uranium may be present in the soil as the divalent uranyl ion, UO_2^{2+}, and will be mobile in soils if present as the uranyl ion.

Masuda and Yamamoto (1971) examined the desorption of uranium from alluvial, sand and volcanic ash soils. The cation exchange capacities were 13.7, 7.7 and 33.0 meq/100 g, respectively, for the alluvial sand and volcanic ash soils. Strong salt solutions and distilled water were used as leachates. Loads of more than 2000 μg U/g of soil were required before desorption by distilled water was 1% of the uranium on the soils. The uranium was amended to the soils as uranyl nitrate before the desorption work. Desorption of uranium was higher with 0.5M $(NH_4)_2SO_4$, 1.34M KCl and 1.44M K_2HPO_4 salt solutions, but reached 50% removal only for the alluvial soil with a high adsorbed uranium content in 1.44M K_2HPO_4 solution. The volcanic ash soil did not attain 5% uranium desorbed in any of the salt solutions.

The effects of carbonate ions on uranium desorption from soils was examined by Yamamoto et al. (1973). They used an alluvial soil, a volcanic ash soil and a sandy soil containing up to 500 μg U/g air-dried soil in their desorption experiments. The desorption of uranium declined as a power function of the amount of uranium on the soil. Desorption results are shown in Table 3-100. Ten grams of soil were magnetically stirred with 100 ml of potassium carbonate solution for 30 min and stood overnight before filtering and a fluorometric uranium analysis. As can be seen in Table 3-92, uranium desorption was very low in the presence of low to moderate environmental carbonate concentrations.

TABLE 3-100. DESORPTION OF URANIUM FROM SOILS WITH DISTILLED WATER AND CARBONATE SOLUTIONS (YAMAMOTO, 1973)

Soil	U Content, μg/g	Distilled Water, %	Carbonate Solution, % 4.3mg CO_3^{-2}/l	Carbonate Solution, % 43.4mg CO_3^{-2}/l
Alluvial	7.1	0.31	0.62	1.20
	485.0	0.22	0.25	0.41
Sandy	10.1	0.14	0.27	0.90
	488.2	0.12	0.13	0.46
Volcanic Ash	8.3	0.18	0.57	1.15
	500.0	0.09	0.10	0.20

Dall'Aglio et al. (1974) discussed some of the geochemical processes responsible for precipitating secondary uranium minerals. There are a series of processes capable of bringing about a very effective separation and concentration of uranium. The most important process is the attainment of high UO_2^{+2} activity in circulating waters because of low concentration or depletion of CO_3^{-2} which is the most effective uranyl complexing agent. The microorganisms involved were soil microflora and bacteria of mine-waters and granites. Some species were identified. Batch cultures were used to study uranium insolubilization involving biodegradation of uranium complexing organic compounds. The authors suggested that the redeposition of uranium by bacteria may be the origin of some uranium deposits.

Uranium solubilization and insolubilization from granites by heterotrophic bacteria were investigated by Magne et al. (1974). Microbial activity increased the solubilization of uranium from 2 to 97 times by biosyntheses of complexing and chelating compounds.

Grandstaff (1976) arrived at a rate expression for the effects of surface area and uraninite composition, oxygen content of the solution, carbonate content, organics content, pH and system temperature on uraninite dissolution. R, the rate of uraninite (UO_2) dissolution = $\frac{-d(\text{uran})}{dt} = 10^{20.25} (SS)(RF)^{-1} (10^{3.38-10.8\ NOC}) (a\Sigma CO_2) (D.O.) (a_{H+}) \exp(-7045/T) \text{day}^{-1}$, where SS is the specific surface area (cm^2/g), RF is an organic retardation factor, NOC is the mole fraction of nonuranium cations in the uraninite, D.O. is the dissolved oxygen content of the water (ppm), CO_2 is the total dissolved carbonate and T is the absolute temperature. The rate expression was used to predict UO_2 dissolution rates under varying conditions in the absence of organics in the contacting water with good results. Dissolved inorganic species in artificial seawater other than hydrogen ion activity (pH), total carbonate and dissolved oxygen did not appreciably affect the UO_2 dissolution rate. The organic retardation factor must be determined experimentally for each organic-containing solution by comparing the calculated UO_2 dissolution rate without organics in the environment with the observed dissolution rate, or RF = R calculated/R observed. Retardation values of up to 420 were obtained. The magnitude of the affects of the several factors in the expression on the oxidation rate of U(IV) to U(VI) could be of assistance in understanding uranium mobility in soil and rock environments.

Summary

The common oxidation states of uranium are U(III), U(IV), U(V) and U(VI) (Udaltsova, 1963). However, in the geologic environment U(IV) and U(VI) are the most important oxidation states. In oxidizing environments U(VI) compounds such as KUO_2VO_4 (Garrels and Christ, 1965), $UO_2NH_4PO_4$, Na_2UO_4 and UO_2KPO_4 (Figure 3-26) are stable and can precipitate. U(IV) would precipitate as UO_2 in a reducing environment. U(VI) solution species govern uranium concentrations and movement in oxidizing environments (Figure 3-27). Uranium retention by soils and rocks in alkaline conditions is poor because the predominant uranium species at $pH > 6$ in oxidizing environments (Figure 3-27) are either neutral or negatively charged. An increase in CO_2 pressure in soil solutions reduces uranium adsorption and can increase uranium concentration. The cation exchange properties of soils could contribute to the adsorption of uranium in the neutral to acidic pH range due to the presence of UO_2^{2+}. Oxidation-reduction conditions and pH would be important parameters of uranium mobilization and immobilization.

The above theoretically based predictions are substantiated by experimental results. Uranium has been reported to be solubilized and highly mobile in carbonate-containing waters (Brown and Keller, 1952; Naumov, 1961; Ermolaev et al., 1965; Legin et al., 1966; Haglund, 1968, 1969). Soluble uranium [U(VI)] can:

1. precipitate in the presence of phosphorus as evidenced by a direct correlation of uranium and phosphate content in soils and rocks (Bell, 1960; Sakanoue, 1960; Habashi, 1962; Kuznetsov et al., 1968; Menzel, 1968; Mihalik, 1968), and
2. be adsorbed by the soil organic component and/or reduced to U(IV) followed by precipitation (Breger et al., 1955; Kolodny, 1969; Kolodny and Kaplan, 1970; Baturin, 1971; Dall'Aglio, 1971; Dorta and Rona, 1971; Gabelman, 1971: Baturin and Kochenov, 1973; Mo et al., 1973).

An increase in uranium content with a decrease in soil or sediment particle size was reported by several workers (Kovalevskii, 1967; Mizuno and Mochizuki, 1970; Ritchie et al., 1972).

The uranyl ion can be adsorbed on clay minerals (Goldsztaub and Wey, 1955; Kovalevskii, 1967; Rubtsov, 1972; Ritchie et al., 1972; Rancon, 1973) and other adsorbent materials (Masuda and Yamamoto, 1971; Yamamoto et al., 1973), but also is inclined to form complexes with anions, such as carbonate, that are commonly found in the soil solution (Figure 3-27). Uranyl salts also have been shown to substitute for Ca^{2+} during replacement of calcite by apatite (Ames, 1960), and Ca^{2+} competes with UO_2^{2+} for available sites during ion exchange reactions on inorganics such as calcite (Rancon, 1973) resulting in low uranium Kd values. However, uranyl ion adsorption on organic materials and humic substances is quite high (Szalay, 1954, 1957; Manskaya et al., 1956; Rozhkova et al., 1959; Rancon, 1973) especially at acid pH values. The most important parameters of uranium migration and retention are system Eh and pH.

References

Adams, J. A. S., J. K. Osmond, and J. J. W. Rogers. 1959. The Geochemistry of Uranium and Thorium. Phys. Chem. Earth. 3:298.

Ames, L. L., Jr. 1960. Some Cation Substitutions During the Formation of Phosphorite from Calcite. Economic Geology. 55:354-362.

Baturin, G. N. 1971. Uranium in Solutions of Ooze Deposits in the Southeastern Atlantic. Dokl. Akad. Nauk. SSSR. 198:1186-1188 (in Russian).

Baturin, G. N. and A. V. Kochenov. 1973. Uranium in Interstitial Waters of Marine and Oceanic Sediments. Geokhimiya. No. 10:1529-1536 (in Russian).

Bell, K. G. 1960. Deposition of Uranium in Salt-Pan Basins. U.S.G.S. Professional Paper No. 354-G:161-169.

Breger, I. A., M. Deul, and S. Rubinstein. 1955. Geochemistry and Mineralogy of a Uraniferous Lignite. Econ. Geol. 50:206-226.

Brown, J. H. and W. D. Keller. 1952. Uranium in the Clay of a Black Radioactive Shale. Science. 116:632-633.

Clark, S. P., Jr., Z. E. Peterman and K. S. Heier. 1966. Abundances of Uranium, Thorium, and Potassium. IN: Handbook of Physical Constants. S. P. Clark (ed.). Geol. Soc. Am. Mem. 97.

Dall'Aglio, M. 1971. Study of the Circulation of Uranium in the Supergene Environment in the Italian Alpine Range. Geochim. et Cosmochim. Acta. 35:47-59.

Dall'Aglio, M., R. Gragnani, and E. Locardi. 1974. Geochemical Factors Controlling the Formation of the Secondary Minerals of Uranium. IAEA-SM-183/21. pp. 33-48.

Dement'yev, V. S. and N. G. Syromyatnikov. 1968. Conditions of Formation of a Sorption Barrier to the Migration of Uranium in an Oxidizing Environment. Geochemistry International. 5:394-400.

Dorta, C. C. and E. Rona. 1971. Geochemistry of Uranium in the Cariaco Trench. Bull. Mar. Sci. 21:754-765.

Ermolaev, N. P., A. P. Zhidikora, and V. A. Zarinski. 1965. On the Silicate Form of Uranium Transport in Aqueous Solutions. Geokhimiya No. 7:813-826 (in Russian).

Fairbridge, R. W. (ed.). 1972. The Encyclopedia of Geochemistry and Environmental Sciences. Van Nostrand Reinhold Company.

Gabelman, J. W. 1971. Sedimentology and Uranium Prospecting. Sediment. Geol. 6:145-186.

Garrels, R. M. and C. L. Christ. 1965. Solutions, Minerals, and Equilibria. Harper and Row, New York.

Goldsztaub, S. and R. Wey. 1955. Adsorption of Uranyl Ions by Clays. Bull. Soc. Franc. Mineral. Crist. 78:242.

Grandstaff, D. E. 1976. A Kinetic Study of the Dissolution of Uraninite. Econ. Geol. 71(8):1493-1506.

Habashi, F. 1962. Correlation Between the Uranium Content of Marine Phosphates and Other Rock Constituents. Econ. Geol. 57:1081-1084.

Haglund, D. S. 1968. The Distribution of Uranium in Recent Carbonate Sediments and Skeletons of Organisms and the Effect of Diagenesis on Uranium Redistribution. Rensselaer Polytechnic Institute. Thesis.

Haglund, D. S., G. M. Friedman, and D. S. Miller. 1969. The Effect of Freshwater on the Redistribution of Uranium in Carbonate Sediments. J. Sediment. Petrol. 39:1283-1296.

Harriss, R. C. and J. A. S. Adams. 1966. Geochemical and Mineralogical Studies on the Weathering of Granitic Rocks. Am. J. Science. 264:146-173.

Horráth, E. 1960. Investigations of Uranium Adsorption to Peat in Natural Waters Containing U-Traces. Magyar Tudomanyos Akad. Atommag Kutató Intézete, Kőzlemenyek. 2:177-183 (in Hungarian).

Kolodny, Y. 1969. Studies in Geochemistry of Uranium and Phosphorites. University of California. Thesis.

Kolodny, Y. and I. R. Kaplan. 1970. Deposition of Uranium in the Sediment and Interstitial Water of an Anoxic Fjord. CONF-700965-1.

Kovalevskii, A. L. 1967. Dependence of the Content of Some Trace Elements on the Clayiness of Soils. Mikroelem. Biosfere Ikh Primen. Scl. Khoz. Med. Sib. Dal'nego Vostoka, Dokl. Sib. Knof., 2nd. 1964. O. V. Makew. Buryat. Khizhn. Izd. Ulan-Ude, USSR.

Kuznetsov, Y. V., Z. N. Simonyak, A. P. Lisitsyn, and M. S. Frenklikh. 1968. Thorium Isotopes (^{230}Th, ^{232}Th) in the Surface Layer of the Indian Ocean Sediments. Geochem. Int. 5:169-177.

Latimer, W. M. 1952. The Oxidation States of the Elements and Their Potentials in Aqueous Solutions. Second Edition. Prentice-Hall, Inc., Englewood Cliffs, NJ.

Legin, V. K., Y. V. Kuznetsov and K. F. Lazarev. 1966. Uranium Occurrence in Marine Sediments. Geokhimiya No. 5:606-608 (in Russian).

Magne, R., J. R. Berthelin, and Y. Dommergues. 1974. Solubilization and Insolubilization of Uranium from Granites by Heterotrophic Bacteria. IN: Formation of Uranium Ore Deposits. IAEA-SM-183/18, p. 73.

Manskaya, S. M., G. V. Drozdora, and M. P. Yemel'yanova. 1956. Fixation of Uranium by Humic Acids and Melanoidins. Geokhimiya. No. 4.

Masuda, K. and T. Yamamoto. 1971. Studies on Environmental Contamination by Uranium. II. Adsorption of Uranium on Soil and Its Desorption. J. Radiat. Res. 12:94-99.

Menzel, R. G. 1968. Uranium, Radium, and Thorium Content in Phosphate Rocks and Their Possible Radiation Hazard. J. Agr. Food Chem. 16:231-34.

Mihalik, P. 1968. Uranium Compounds in the Dominion Reefs, and Their Association with Phosphorus Compounds. NIM-415.

Mizuno, A. and T. Mochizuki. 1970. Distribution of Uranium in the Sediments from San'in Off-Shore, Southwestern Japan. Chishitsu Chosasho Geppo. 21:287-292 (in Japanese).

Mo, T., A. D. Suttle, and W. M. Sackett. 1973. Uranium Concentrations in Marine Sediments. Geochim. et Cosmochim. Acta. 37:35-51.

Naumov, G. B. 1961. Some Physico-Chemical Peculiarities of Uranium Behavior in Hydrothermal Solutions. Geokhimiya. No. 2:115-132 (in Russian).

Palei, P. N. (comp.). 1962. Analytical Chemistry of Uranium. Trans. by N. Kaner. 1963. Israel Program for Scientific Translations Ltd. 421 p.

Racon, D. 1973. The Behavior in Underground Environments of Uranium and Thorium Discharged by the Nuclear Industry. IN: Environmental Behavior of Radionuclides Released in the Nuclear Industry. IAEA-SM-172/55. pp. 333-346 (in French).

Ritchie, J. C., P. H. Hawks, and J. R. McHenry. 1972. Thorium, Uranium, and Potassium in Upper Cretaceous, Pateocene, and Eocene Sediments of the Little Tallahatchie River Watershed in Northern Mississippi. Southeast Geol. 14:221-231.

Rozhkova, Ye.V., Ye. G. Razumnaya, M. B. Serebryakova and O. V. Shchebak. 1959. Role of Sorption in Concentration of Uranium in Sedimentary Rocks. Tr. II. Mezhdunar, knof. po miro nmu ispol'z. atom. energii. 3.

Rubtsov, D. M. 1972. Thorium and Uranium Content in the Clay Fraction of Podzolic Mountain Soils of Thin Forests. Radioekol. Issled Prir. Biogeotsenozakh. pp. 53-66 (in Russian).

Sakanoue, M. 1960. Geochemical Studies on the Radioactive Sediments. II. Uranium Content of Natural Waters from the Ningyo-Pass Mining Area. Nippon Kagakii Zasshi 81:896-898.

Sakanoue, M. 1960. Geochemical Studies on the Radioactive Sediments. III. Uranium, Phosphorus, and Arsenic in the Sedimentary Bed at Ningyo Pass. Nippon Kagaku Zasshi 81:898-902.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Seaborg, G. T. and J. J. Katz (ed.). 1954. The Actinide Elements. McGraw Hill Book Company, Inc.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal Ion Complexes. Second ed. Spec. Publ. No. 17. The Chemical Society, London.

Starik, I. Ye., F. Ye Starik and A. N. Apollonova. 1958. Adsorption of Traces of Uranium on Iron Hydroxide and Its Desorption by the Carbonate Method. Zh. Neorgan. Khimii. 3(1).

Szalay, A. 1954. The Enrichment of Uranium in Some Brown Coals in Hungary. Acta Geol. Acad. Sci. Hungary. 2:299-311.

Szalay, A. 1957. The Role of Humus in the Geochemical Enrichment of U in Coal and Other Bioliths. Acta Phys. Acad. Sci. Hungary. 8:25-35.

Udaltsova, N. I. 1963. General Information on Uranium. IN: Analytical Chemistry of Uranium. Israel Program for Scientific Translations. pp. 3-7.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau.

Weast, R. C., Editor. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio. pp. B344-B345.

Yakobenchuk, V. F. 1968. Radioactivity and Chemical Properties of Sod-Podzolic Soils in the Ukranian Western Polesie. Visn. Sil's Kogosped. Nauki. 11:45-50 (in Ukranian).

Yamamoto, T., E. Yunoki, M. Yamakawa, and M. Shimizu. 1973. Studies on Environmental Contamination by Uranium. 3. Effects of Carbonate Ion on Uranium Adsorption to and Desorption from Soils. J. Radiat. Res. 14:219-224.

ZIRCONIUM

Natural Soil and Rock Distributions

The zirconium distribution and content in igneous and sedimentary rocks are shown in Table 3-101. It should be noted that much of the zirconium contained in sedimentary rocks is present as resistate material such as zircon ($ZrSiO_4$), which is very slightly soluble in any aqueous solution. The average content of worldwide soils is given by Vinogradov (1959) as 300 ppm zirconium.

TABLE 3-101. THE AVERAGE ZIRCONIUM CONTENT OF ROCKS (TUREKIAN AND WEDEPOHL, 1961)

Rock Type	Zr, ppm
Igneous Rocks	
Ultramafic	45
Basaltic	140
Granitic, high Ca	140
Granitic, low Ca	175
Syenite	500
Sedimentary Rocks	
Shale	160
Sandstone	220
Limestone-dolomite	19

Brief Chemistry

Eighteen isotopes and two isomers of zirconium are known. The naturally occurring isotopes are listed in Table 3-102. All are stable except ^{96}Zr which has a half-life listed as $>3.6 \times 10^{17}$ years (Weast, 1976). For all practical purposes, ^{96}Zr also is a stable isotope.

The immediate concern in radioactive waste disposal is for ^{95}Zr with a relatively short half-life of 65 days. Also obtained in much smaller yields as a fission product is the longer-lived ^{93}Zr (half-life 1.5×10^6 years) which is of long-term interest (Schneider and Platt, 1974). ^{95}Zr decays by β^- emission to ^{95}Nb which also emits a β^- and decays to stable ^{95}Mo.

TABLE 102. NATURAL ISOTOPES OF ZIRCONIUM AND THEIR ABUNDANCES (WEAST, 1976)

Isotope	Abundance, %
^{90}Zr	51.46
^{91}Zr	11.23
^{92}Zr	17.11
^{94}Zr	17.40
^{96}Zr	2.80

The most stable and common form of zirconium in rocks is as the simple orthosilicate zircon, $ZrSiO_4$. The only oxidation state of zirconium of any importance in aqueous solutions is Zr(IV), though usually not as Zr^{+4} cations. Due to the high charge and a small atomic radius (0.72 Å in six-fold coordination, 0.84 Å in octahedral coordination, Shannon and Prewitt, 1969), zirconium ions are readily hydrolyzed in aqueous solutions. When an acid solution is neutralized with a base such as NH_4OH, hydrous zirconium oxide is precipitated rather than zirconium hydroxide (Blumenthal, 1958). Zirconium compounds, such as $ZrCl_4$, react violently with water, producing high acidity solutions. A zirconyl salt ($ZrOCl_2 \cdot 8H_2O$) is produced with liberation of hydrogen ions. A solution 0.05M in $ZrOCl_2 \cdot 8H_2O$, for example, has a pH of 1. The equilibrium established is $Zr^{+4} + nH_2O \rightarrow Zr(OH)_n^{4-n} + nH^+$ and depends on the solution acidity.

According to Connick and McVey (1949), in 2.0 to 0.2M perchloric acid at 25°C, zirconium exists as Zr^{+4} and $Zr(OH)^{+3}$ ions. At concentrations of perchloric acid of less than 0.2M, the zirconium species was probably $Zr(OH)_2^{+2}$. At or above 2.0M $HClO_4$, zirconium exists exclusively as Zr^{+4} ions (Larsen and Wang, 1954). When zirconium hydroxides are acidified with HCl, oxo cations (ZrO^{+2}) first appear, and not until the solution is 2N in HCl or higher, do appreciable amounts of Zr^{+4} ions appear (Lister and McDonald, 1951).

Zirconium forms very stable complexes with halogens of the type M_2ZrG_6 where M is a univalent metal and G is a halogen. Zirconium also forms a series of complexes with fluoride phosphate and sulfate ions and many of the organic ligands. Electrolysis of a solution of $Zr(SO_4)_2 \cdot 2H_2O$, for example, produces hydrogen at the cathode and zirconium sulfate at the anode. Hence, the compound was H_2 [$ZrO(SO_4)_2$], with zirconium in the complex anion [$ZrO(SO_4)_2$]$^{-2}$. Since most of the waste solutions containing zirconium are near-neutral solutions, no Zr^{+4} ion should exist in solution. There are only charged to neutral polymers and complexes of zirconium existing in the pH range of most radioactive waste solutions.

Solid Phase and Solution Equilibria

The zirconium minerals in increasing order of stability are: $Zr(OH)_4$, ZrO_2, and $ZrSiO_4$, as shown in Figure 3-28. The thermodynamic data for $Zr(OH)_4$, ZrO_2 and $ZrSiO_4$ were obtained from Sillen and Martell (1964), Baes and Mesmer (1976) and Wagman et al. (1971), respectively. The most stable mineral throughout the pH range is zircon ($ZrSiO_4$). This is consistent with the empirical observations of many geologists and soil scientists who find that zircon ($ZrSiO_4$) is ubiquitous in soils and is very stable even compared to other common soil minerals.

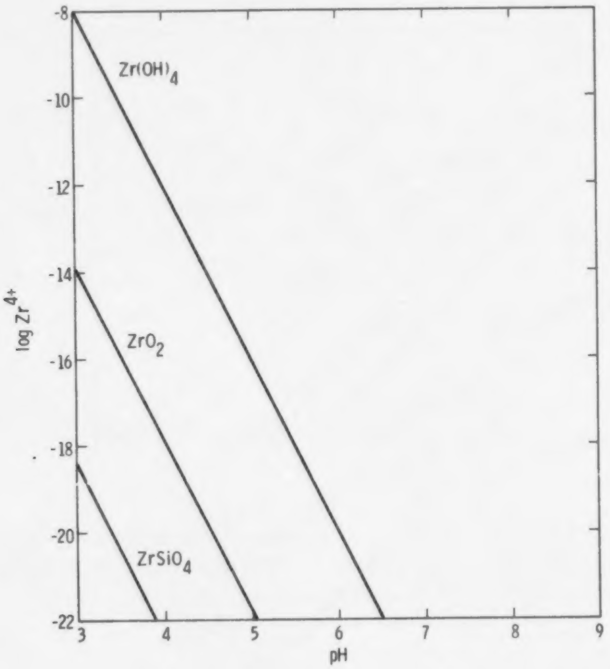

Figure 3-28. The stability of zirconium solids at 25°C and in equilibrium with soil silica ($pH_4SiO_4^\circ = 3.1$).

The activity of various solution species with the change in pH and in equilibrium with zircon ($ZrSiO_4$) and soil SiO_2 is given in Figure 3-29. The thermodynamic data for all the hydrolysis species were selected from Baes and Mesmer (1976). Other solution species data were selected from Sillen and Martell (1964). Zirconium forms complexes with the common soil anions (F^-, Cl^-, SO_4^{2-}, NO_3^-). The significance of complexation of zirconium with these anions decreases in the following order: F^-, SO_4^{2-}, Cl^-, NO_3^-. Although zirconium forms complexes with common soil anions, ZrF^{3+} complex would be the only one which could contribute significantly in acidic environments (pH 3.5) to the total zirconium in solution. It can be seen from the diagram that the uncomplexed zirconium (Zr^{4+}) would exist in significant amounts only in very acidic solutions (pH <1). The zirconium ions are hydrolyzed in solutions with pH values of greater than 1.0. The most dominant zirconium solution species with the conditions assumed in Figure 3-29 are ZrF^{3+}, $Zr(OH)_4^\circ$, and $Zr(OH)_5^-$ in pH ranges of <3.5, 3.5-6.25, and >6.25, respectively.

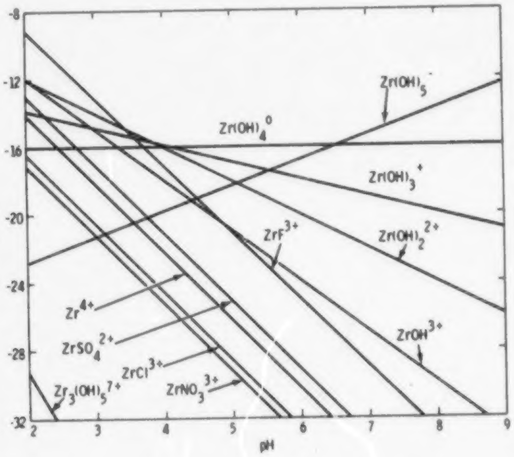

Figure 3-29. The activity of various zirconium species in equilibrium with zircon [$ZrSiO_4(s)$] and soil solution silica ($pH_4SiO_4 = 3.1$) at $pCl^- = pSO_4^{2-} = 2.5$, $pNO_3^- = 3.0$ and $pF^- = 4.5$.

If a waste solution containing zirconium is assumed to be in equilibrium with zircon and the conditions assumed in Figure 3-29, then the total activity of zirconium in solution would be lower than 10^{-14} over a pH range of 3.5 to 8.

The Zr^{4+} ion becomes increasingly hydrolyzed above pH 1 (Figure 3-29). The Zr^{4+} content of the soil solution falls rapidly, as does the content of fluoride complex ZrF^{3+}, in favor of hydrolyzed species at higher pH values. Only at relatively low pH values of less than 4 do positively charged species of zirconium predominate. Because most soils and rocks buffer waters contacting them to pH 5 or higher, ion exchange probably plays a relatively minor role in zirconium retention by soils and rocks. Because of the formation of negatively charged complexes in solutions of pH >6.5 (Figure 3-29), zirconium adsorption would be expected to decrease with an increase in pH above 6.5.

Experimental Adsorption Results

Rhodes (1957) determined the effect of pH on the distribution coefficient of zirconium-niobium on a Hanford soil. The soil was made up of 2% $CaCO_3$ with >2 mm diameter material, 6%; 2 to 0.2 mm diameter material, 67%; 0.02 to 0.2 mm diameter material, 19%; 0.02 to 0.002 mm diameter material, 6%; and <0.002 mm diameter material, 2%. The cation exchange capacity was 5 meq/100 g and the water paste pH was 8.6. The bulk of the soil consisted of quartz, feldspars, augite, olivine and mica. The clay fraction contained mainly montmorillonite. The Kd values for zirconium as a function of pH are given in Table 3-103.

TABLE 3-103. ZIRCONIUM-NIOBIUM Kd VALUES AS A FUNCTION OF pH (RHODES, 1957)

pH	Kd, ml/g	pH	Kd, ml/g
0	82	8.3	282
1	1028	9.6	90
2.6	1340	10.2	104
4.1	>1980	11.0	180
6.4	>1980	12.2	>1980
7.7	>1980	14.0	>1980

Rhodes considered that the dips in zirconium Kd for pH 8 to 12 were due to a charge alteration of the zirconium polymer or colloid within this pH range.

Dlouhy (1967) gave Kd values for zirconium on Casaccia soil and Casaccia tuff from CNEN, Italy. The soil and tuff were not characterized. The range of zirconium Kd values given for the soil was 130 to 150 ml/g and for the tuff, 260 to 350 ml/g.

Benson (1950) reported a visible, white precipitate in systems containing 3×10^{-2}M zirconium. The uptake of trace ^{95}Zr was not appreciably different from that noted in the presence of carrier indicating that precipitation also occurred at the trace concentration. Zirconium was not appreciably affected by the presence of other cations unless the pH was below 2. Benson also reported that carbonate, oxalate and citrate ions inhibited zirconium uptake on soil over a wide pH range, probably because of the formation of complex anionic species.

Sorathesn et al. (1960) stated that ^{95}Zr behaved like a colloid at pH 6 to 9. They reported the zirconium Kd on illite at 7 days equilibration time to be 24,470 ml/g.

Prout (1959) reported that tests made at pH 4 with 10^{-3}M $C_2O_4^{-2}$ showed adsorption of zirconium-niobium on soil to be inhibited, but at pH 8, the oxalate did not seriously affect the removal of zirconium-niobium. Schulz (1965) reported that zirconium and niobium were two of the elements that were adsorbed by soil in a very immobile form.

Arnold and Crouse (1971) determined the adsorption of fission products on copper ore produced by nuclear fracturing. The copper leach solution was pH 1.2 to 1.8 with H_2SO_4 and at 85°C. The copper ore was in 2.5 kg, 4-in. columns with 2000 g of radioactive rubble from a nuclear shot added between 500 g layers of minus 1/2-in. copper ore. Sulfuric acid was added during the run to assure that pH values stayed below 2. Almost none of the ^{95}Zr-^{95}Nb was found in the column effluent because it was strongly adsorbed by the ore. When a second run was made with the fission products, including ^{95}Zr-^{95}Nb added in soluble form, the adsorption results were the same. Zirconium Kd values of 50 to 60 ml/g were obtained on batch equilibria from pH 1.5 to pH 2.8.

Migration Results

Field Studies--

Spitsyn et al. (1958) used an alkaline solution (4 to 8 g NaOH/1, 200 g $NaNO_3$/1) and an acidic solution [6 to 8 g HNO_3/1, 200 g $Al(NO_3)_3$/1] in laboratory and field studies of radionuclide migration rates. Zirconium was adsorbed and retained by a sand in field tests near the point of injection of the waste solutions for both the acidic and alkaline solutions. Little movement was indicated even under acidic conditions.

Magno et al. (1970) investigated the radionuclides from the Nuclear Fuel Services plant in western New York that were migrating through the plant effluent lagooning system. They estimated that greater than 90% of the ^{95}Zr discharged from the plant was deposited by sedimentation in the lagoon system.

Brookins (1976) reported that fission product zirconium was retained in the shale very near to areas of generation in the natural reactor at Oklo.

Laboratory Studies--

Fallout material on soil from an underground nuclear explosion was used by Essington et al. (1965) to determine the leaching effects of water, HCl and chelating agents. The soil was suspended in 25 ml of solution and equilibrated for up to 106 days. The 10^{-4} molar chelating agents in solution included sodium-diethylenetriaminepentaacetate, sodium-cyclohexane-1,2-diaminetetraacetate, sodium-ethylenediamine di(o-hydroxyphenylacetate) and 0.1M HCl. ^{95}Zr-^{95}Nb was identified in the original soil. Chelating agents, HCl and water equilibrations did not appreciably increase ^{95}Zr-^{95}Nb solubility. In column studies with Yolo soil (pH 7.9), Sorrento soil (pH 7.8) and Hanford soil (pH 6.6), water and calcium-diethylenetriaminepentaacetate (10^{-4}M) leaches of 7 days produced no detectable ^{95}Zr-^{95}Nb in the effluent solution. The dominant clay minerals in the Hanford, Sorrento and Yolo soils were illite, kaolinite and montmorillonite.

According to Schulz (1965), the zirconium in soils is either very strongly adsorbed by the clay particles or is present as an insoluble oxide or hydroxide. In either case, the zirconium in the soil is immobile.

Eichholz et al. (1967) investigated the partitioning of dissolved radionuclides between suspended sediment particles and aqueous solutions. Several natural water samples were characterized and used in the adsorption studies as suspended solids sources (see Table 3-30). A fission product mixture was added to the natural water samples, the system equilibrated and the water recovered and filtered. The adsorption of ^{95}Zr and daughter ^{95}Nb are shown in Table 3-104. A large portion of the zirconium was associated with the particulate matter in a highly concentrated form.

TABLE 3-104. ADSORPTION OF ^{95}Zr AND ^{95}Nb ON SUSPENDED SOLIDS IN NATURAL WATERS (EICHHOLZ ET AL., 1967)

Source	Suspended Solids, mg/ℓ	^{95}Zr Adsorption, %	^{95}Nb Adsorption, %
Colorado River	229	61.1	33.3
Camp McCoy	12	50.0	4.7
Bayou Anacoco	24	80.5	23.8
Lodgepole Creek	965	81.3	-
Chattahoochee River	131	88.4	18.9
Billy's Lake	8	53.9	8.9

Adsorption does not appear to be a direct function of suspended solids content but has to include a consideration of dissolved solids content, pH and solids composition before the adsorption results begin to make any sense. The high ^{95}Zr adsorption on Chattahoochee River suspended solids was due to the low dissolved solids content (31 ppm), which suggests that a positively charged zirconium species was involved.

Harrison (1969), using nuclear debris contaminated with ^{95}Zr-^{95}Nb as a source, approached equilibrium from the direction of starting with the radionuclide on the solid. The leaching produced ^{95}Zr-^{95}Nb Kd values of 5,200 to 17,000 ml/g in distilled water as a function of particle size range (<4000 to <62 μm), 790 to 2700 ml/g in synthetic seawater for the same particle size range and 270 to 1200 ml/g in 1M ammonium acetate for that particle size range. An implication of this work is that cation exchange is involved because the ^{95}Zr-^{95}Nb Kd values are sensitive to competing ion concentrations.

Summary

Trace concentrations of zirconium are strongly adsorbed on soils at pH 1 or higher with a dip in Kd values between pH 8 to 12 (Rhodes, 1957), probably due to the prevalence of uncharged or anionic zirconium species over this pH range (Figure 2-14). There is some evidence for affects caused by competing cations at near-neutral pH, suggesting at least partial removal by an ion exchange mechanism of polymerized or colloidal species (Eichholz et al., 1967; Harrison, 1969). Zirconium is well-adsorbed by the soil over the normal pH range of 4 to 8 (Spitsyn et al., 1958; Schulz, 1965; Magno et al., 1970). Carbonate, oxalate and citrate complexes of zirconium have been reported to migrate rapidly through soil columns (Bensen, 1960).

References

Arnold, W. D. and D. J. Crouse. 1971. Radioactive Contamination of Copper Recovered from Ore Fractured with Nuclear Explosions. ORNL-4677.

Baes, C. F., Jr. and R. F. Mesmer. 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.

Benson, D. W. 1960. Review of Soil Chemistry Research at Hanford. HW-67201.

Blumenthal, W. B. 1958. The Chemical Behavior of Zirconium. Van Nostrand Company, Inc.

Brookins, D. G. 1976. Shale as a Repository for Radioactive Waste: The Evidence from Oklo. Environmental Geology. 1:255-259.

Connick, R. E. and W. H. McVey. 1949. The Aqueous Chemistry of Zirconium. J. Am. Chem. Soc. 71:3182-3192.

Dlouhy, Z. 1967. Movement of Radionuclides in the Aerated Zone. IN: Disposal of Radioactive Wastes into the Ground. IAEA-SM-93/18.

Eichholz, G. G., T. F. Craft, and A. N. Galli. 1967. Trace Element Fractionation by Suspended Matter in Water. Geochim. et Cosmochim. Acta. 31:737-745.

Essington, E. H., H. Nishita and A. J. Steen. 1965. Release and Movement of Radionuclides in Soils Contaminated with Fallout Material from an Underground Thermonuclear Detonation. Health Physics. 11:689-698.

Harrison, F. L. 1969. Radioactive Debris from Underground Nuclear Explosions: 1. Physical and Chemical Characteristics, 2. Biological Availability of the Radionuclides to Aquatic Animals. UCRL-50596.

Magno, P., T. Reavy, and J. Apidianakis. 1970. Liquid Waste Effluents from a Nuclear Fuel Reprocessing Plant. BRH-NERHL-70-2.

Larsen, E. M. and P. Wang. 1954. The Ion Exchange of Zirconium and Hafnium in Perchloric Acid with Amberlite IR-120. J. Am. Chem. Soc. 76:6223-6229.

Lister, B. and L. McDonald, 1951. Some Aspects of the Solution Chemistry of Zirconium. AERE-C/R-801.

Prout, W. E. 1959. Adsorption of Fission Products by Savannah River Plant Soil. DP-394.

Rhodes, D. W. 1957. The Effect of pH on the Uptake of Radioactive Isotopes from Solution by a Soil. Soil Science Society America, Proceedings. 21:389-392.

Schneider, K. J. and A. M. Platt. 1974. High-Level Radioactive Waste Management Alternatives. BNWL-1900, Vol. I.

Schulz, R. K. 1965. Soil Chemistry of Radionuclides. Health Physics. 11:1317-1324.

Shannon, R. D. and C. T. Prewitt. 1969. Effective Ionic Radii in Oxides and Fluorides. Acta Cryst. B. 25:925.

Sillen, L. G. and A. E. Martell. 1964. Stability Constants of Metal-Ion Complexes. Special Publication No. 17. The Chemical Society, London.

Sorathesn, A., G. Bruscia, T. Tamura, and E. G. Struxness. 1960. Mineral and Sediment Affinity for Radionuclides. CF-60-6-93.

Spitsyn, V. I., V. D. Balukova, A. F. Naumova, V. V. Gromov, F. M. Spiridonov, E. M. Vetrov, and G. I. Gravfov. 1958. A Study of the Migration of Radioelements in Soils. IN: Proc. Second Annual U.N. Conf. Peaceful Uses of Atomic Energy. 18:439-448.

Turekian, K. K. and K. H. Wedepohl. 1961. Distribution of the Elements in Some Major Units of the Earth's Crust. Bull. Geol. Soc. Am. 72:175-192.

Vinogradov, A. P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils. Consultants Bureau.

Wagman, D. D., W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, R. H. Schumm, and K. L. Churney. 1971. Selected Values of Chemical Thermodynamic Properties. Tables for Elements 54 Through 61 in the Standard Order of Arrangement. NBS Technical Note 270-5.

Weast, R. C. 1976. Handbook of Chemistry and Physics. The Chemical Rubber Co.

SECTION 4

CONCLUSIONS AND EVALUATION

The available data on interaction of various elements with the geologic media were collected and discussed in Section 3. At the end of discussions on each element a summary is presented. The information presented in Section 3 will not be repeated here. This section is concerned with general conclusions based upon Section 3. For more details the reader is directed to the previous sections.

The solution ions exist in dynamic equilibrium with soils, sediments, and rocks. Many factors that are inherent to the solid matrix and the solution can influence the concentration of the element and its species in solution. These factors include pH, Eh, CEC, type and amount of soil minerals, solid phases of the element, complexing ligands, and competing ions. In order to determine the distribution of the element between solution and solid and its reactions with the solid matrix, the identity and relative magnitude of the various factors are required. Such information would help predict the solution concentrations of the element and help extrapolate the results to other situations. However, the data presented in Section 3 indicate that there is a general lack of systematic evaluation of various factors that determine element-solid matrix interactions, and no information at present is available to determine the magnitude of the various factors. At best, the available data suggest trends of the influence of some of the factors that control solution concentrations and interaction with solid matrices. This type of information would not be very useful for precisely predicting the general fate of radionuclides in the environment. Additional research required for general understanding of the behavior of radionuclides is outlined at the end of this section.

FACTORS INFLUENCING ADSORPTION OF RADIONUCLIDES ON GEOLOGIC MEDIA

Some of the factors that have been reported to influence the adsorption of elements by geologic media are listed for selected elements in Table 4-1. An "X" indicates that a given factor was reported to influence adsorption of that element (present as a radionuclide). The results reported in Table 4-1 are qualitative only. In most cases, the authors did not definitively show that a specific factor was operative, but hypothesized that it was. Since these data cannot be used for quantitative predictions, they are mainly presented for use as guidelines in future experiments. The probable principal adsorption mechanisms were deduced from an examination of the factors reported for each element. For example, colloid formation is a good indication of precipitation, as pH also may be. An adsorption sensitivity to soil cation exchange capacity, competing ions and system pH usually indicates an ion exchange adsorption mechanism. There is, admittedly, a certain amount of value judgment that went into the summation process because in some cases the literature was ambiguous and vague concerning adsorption-influencing factors, and in other cases, the experimental work has yet to be done. Neptunium and technetium literature data could not be used to determine a probable adsorption mechanism. Adsorption of iodine by organic matter is listed as the adsorption mechanism, but various authors gave conflicting results. However, the majority of the workers reported organic matter to be the principal adsorption media for iodine.

In addition to concentration, the nature of the solution species would have a tremendous effect on the radionuclide interaction with the geologic media and on the mobility of the radionuclides. Very few data are available in the literature delineating species that have been identified in natural environments. Thermodynamic data were used (Section 3) to develop solution species diagrams to predict the predominant solution species. The limitations and drawbacks of this approach are discussed in Section 2. The predicted nature of the predominant solution species of various elements are reported in Table 4-2. The environmental conditions assumed for Table 4-2 data include a pH range of 4 to 9, pO_2 range of 0.68 to 80 atmospheres, pCO_2 of 1.52 to 3.52 atmospheres, $pCl^- = pNO_3^- = pSO_4^{2-} = 3.0$, pF^- 4.5, and $pH_2PO_4^-$ 5.0. It should be pointed out that a change in environmental conditions, in addition to the

TABLE 4-1. FACTORS REPORTED TO EFFECT ADSORPTION OF RADIOELEMENTS OVER THE pH RANGE OF 4 TO 9

	Factors								
						Complex Ions			
Element	pH	Eh	Soil CEC(1)	Competing Ions	Selectively Adsorbed On	Inorganic Ligands	Organic Constituents	Colloid Formation	Probable Adsorption Mechanisms(2)
Am			X	X		X			IE
Sb		X			Iron Oxides	X	X	X	PPT
Ce	X					X	X	X	TE, PPT
Cs			X		Zeolites, Micas				IE
Co	X				Illite, Iron Oxide	X	X	X	IE, PPT
Cm						X		X	PPT
Eu	X			X		X			IE, PPT
I					OM		X		OM
Np						X		X	UNK
Pu	X	X	X			X	X	X	IE, PPT
Pm	X			X			X		IE, PPT
Ra			X	X	Zeolites, Barite				IE
Ru	X				OM	X	X		PPT
Sr	X		X	X	Calcite, Zeolites	X	X		IE
Tc							X		UNK
Th	X		X		OM	X	X	X	IE, PPT
^3H					H_2O				NONE
U	X	X	X		OM	X	X		PPT, IE
Zr	X					X	X	X	PPT

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1. CEC = Cation Exchange Capacity
2. IE = Ion exchange, OM = Organic matter adsorption, PPM = Precipitation, UNK = Unknown.

TABLE 4-2. PREDOMINANT SOLUTION SPECIES OF ELEMENTS(a)

	Predominant Solution Species of Elements		
Elements	Little Affected by Oxidation-Reduction	In An Oxidizing Environment	In A Reducing Environment
Am	Am^{3+}, $AmSO_4{}^+$, $AM(OH)^{2+}$		
Sb		$HSbO_2{}^{\circ}$, $Sb(OH)_3{}^{\circ}$, $SbOF^{\circ}$, $Sb(OH)_4{}^-$	SbO^+
Ce	Ce^{3+}, $CeSO_4{}^+$		
Cs	Cs^+		
Co	Co^{2+}, $Co(OH)_2{}^+$		
Cm	Cm^{3+}, $CmOH^{2+}$, $Cm(OH)_2{}^+$		
Eu	Eu^{3+}, $EuSO_4{}^+$, $Eu_2P_2O_7{}^{2+}$		
I		I^-, $IO_3{}^-$	I^-
Np		$NpO_2{}^+$, $NpO_2HPO_4{}^-$, NpO_2HCO_3	$NpOH^{3+}$, Np^{4+}
Pu		$PuO_2{}^{2+}$, $PuO_2(CO_3)(OH)_2^{2-}$, $PuO_2{}^+$	$PuOH^{2+}$, Pu^{3+}
Pm	Pm^{3+}		
Ra	Ra^{2+}		
Ru		$Ru(OH)_2^{2+}$, $RuO_4{}^-$, $RuO_4{}^{2-}$	$RuO_4{}^-$
Sr	Sr^{2+}		
Tc		$TcO_4{}^-$	TcO_2
Th	ThF^{3+}, $Th(OH)_3{}^+$		
^3H	H^+, $^3H\text{-}O\text{-}H$		
U		UO_2^{2+}, UO_2F^+, $UO_2(OH_2)^{\circ}$, $UO_2(CO_3)_3^{4-}$	UO_2^{2+}, UOH^{3+}, $UO_2{}^+$, $UO_2(CO_3)_3{}^{4-}$
Zr	$Zr(OH)_4{}^{\circ}$, $Zr(OH)_5{}^-$, ZrF^{3+}		

(a) In a pH 4 to 9, pO_2 0.68 to 80, pCO_2 1.52 to 3.52, $pCl^- = pNO_3{}^- = pSO_4{}^{2-} = 3.0$, pF^- 4.5 and $pH_2PO_4{}^-$ 5.0 environment without organic ligands.

ligands not considered in the above assumptions, may change the nature of the solution species. Depending upon the given chemical environment, several species of an element can exist in solution. Cesium, cobalt, promethium, radium, strontium, and tritium would be expected to exist predominantly as uncomplexed solution species as Cs^+, Co^{2+}, Pm^{3+}, Ra^{2+}, Sr^{2+} and $^3H^+$. Certain elements such as plutonium, neptunium and uranium can exist in acidic solutions in an oxidizing environment as uncomplexed solution ions ($PuO_2{}^+$, PuO_2^{2+}, NpO_2^+, UO_2^{2+}). Some of the elements such as curium, thorium and zirconium hydrolyze very readily even in acidic environments, so they mainly exist as hydrolyzed species [$CmOH^{2+}$, $Cm(OH)_2^+$, $Th(OH)_3^+$, $Zr(OH)_4^\circ$, $Zr(OH)_5^-$]. Some of the common soil ligands (CO_3^{2-}, SO_4^{2-}) form strong complexes with americium, curium, europium, neptunium, plutonium and uranium so that these ligands would influence the concentration of these elements in solutions. Oxidation-reduction conditions would predominantly influence the nature of the solution species of antimony, neptunium, plutonium and uranium.

Based upon the nature of the predominant solution species, qualitative predictions regarding the adsorption and movement of various elements can be made. Soils and sediments mainly show cation exchange capacities (since materials carry a large net negative charge) and to a limited extent, anion exchange capacities. Thus, most cations migrate through the soil or rock column at speeds slower than the groundwater. Relative to each other, the trivalent cations generally move the slowest, the divalent cations at intermediate velocities and the monovalent cations most rapidly. Tritium is unique in that it readily substitutes for hydrogen in water and migrates, therefore, at the same velocity as water. Complicating factors include a higher selectivity of a soil or rock component for a given cation or a more successful hydrogen ion competition with one cation relative to another. The relative mobilities of strontium and cesium at low pH is a good example of the latter effect. Strontium is much more mobile at low pH than is cesium.

The simple anions tend to migrate through soils and rocks with little reaction because usually a pH of less than 4 is required to activate a significant soil anion exchange capacity. However, both I and Tc which exist predominantly as anions (I^-, TcO_4^-) undergo other reactions with organic ligands that can greatly slow their migration.

The migration and retention of inorganic complex species (mononuclear and polynuclear) would also be dependent upon the charge and size of the species. Positively charged species would move slower than the negatively charged species. The highly charged metal ions tend to polymerize or form colloidal size, charged precipitates. The trivalent metal ions (Am, Cm, Sb, Ru) and quadrivalent or higher charged metal ions (Pu, Th, U, Zr) are known to form polymers. Initially, at lower pH, the polymers are positively charged and at pH 8 become increasingly negatively charged. The result is good adsorption and very slow movement at acidic to neutral pH, and greatly lessened adsorption and rapid migration from pH 8 upward.

The behavior of organic complexed species of elements is difficult to predict because of the lack of knowledge regarding the exact nature of the organic ligands, a wide variation in amounts and types of organic ligands, and the size and solubility of these organics. These organic materials can either retain the element or complex it in a form that migrates readily. The source of these organic ligands can be the radioactive waste solutions containing the synthetic organic ligands such as TBP and/or the organic ligands produced by soil flora.

The metal ions that take part in replacement reactions depend upon the size and charge of the species involved and the ability of the final mineral product to accept that species into its growing structure. Apatite, for example, accepts into its structure a wide range of metal ions such as strontium, radium, uranium and probably americium and cerium. Cobalt replaces calcium in calcite, and radium and strontium replace barium in barite. These metal ions are buried in the replacement product crystal structure and are effectively retained unless a changing chemical environment causes instability and dissolution of the crystal.

ADDITIONAL RESEARCH NEEDS

The areas that require more work to better understand radionuclide interactions with soil and rock media include:

1. Determination of radionuclide adsorption mechanisms.

Additional work is required in the area of radionuclide adsorption mechanisms (ion exchange, precipitation, coprecipitation). There are many Kd values that include several soil adsorption mechanisms and elemental species operating simultaneously. Definitive experimental data that would allow deduction of probable soil or rock adsorption mechanisms for different elements are lacking in the literature. In addition, the environment in which a given adsorption mechanism predominates should be delineated as well.

2. Factors that influence radionuclide-geologic media interactions.

The influence of different factors (such as pH, Eh, complexing ligands, competing ions, CEC, type and amount of soil minerals, solid phases of element) on the magnitude and extent of adsorption of radionuclides by the geologic media need to be evaluated.

3. An experimental consideration of the effects of redox potential on radionuclide migration.

At depth (below the soil humic zone), where geologic storage has been proposed, the environment is considerably different from that contributing to radionuclide migration on the land surface. There has been minimal examination of the effects on radionuclide migration of the relatively low oxygen partial pressures that will be encountered as a result of geologic waste storage at depth. Many of the igneous rocks comprising a proposed waste repository contain phases such as magnetite, amphiboles or pyroxenes with ferrous iron as a constituent that tends to "buffer" the system at a relatively low oxygen partial pressure until it is all oxidized to ferric iron. The equilibrium partial pressure of oxygen for the reaction, $2Fe_3O_4$ (magnetite) + $1/2\ O_2\ g = 3Fe_2O_3$ (hematite) at 25°C and one atmosphere pressure is $10^{-68.2}$, a reducing environment. Of the 19 elements studied a large change in redox potential would be expected to affect the oxidation states of antimony, neptunium, plutonium, ruthenium, technetium and uranium, hence their solution species and ultimately their migration rate through the surrounding rock.

4. Characterization and influence of organic ligands on radionuclide migration.

The existing thermodynamic data on species are incomplete in many cases, and of dubious quality in other cases. The thermodynamic data should be confirmed by experimental evidence on radionuclide adsorption and migration. Thermodynamic data on the radionuclide complexes with natural soil and water organic components are essentially nonexistent. Note in Table 4-1 that radionuclide reactions with organic material were reported for 12 of the 19 radionuclides reviewed. Hence, what may prove to be a most important influence on radionuclide adsorption and migration is one of the least understood. The sources of organic materials in the environment capable of forming complexed species with radionuclides include the many industrial wastes from various manufacturing processes disposed to the atmosphere and surface waters, the organics included in municipal sewage treatment effluents also disposed to surface waters, the various pesticides and herbicides used during farming operations contained in the atmosphere and irrigation runoff, humic substances and decaying plant and animal remains already present in the soil and rocks along with the associated living soil microflora. With such varied sources and types of organic ligands, a large quantity of work remains to be done in even identifying the metal ligand species involved in radionuclide migration on the land surface.

5. Thermodynamic data determinations for several solids and solution species.

Thermodynamic data are badly needed for several solids and complex solution species of different elements. For example, the ruthenium complexes $RuNO(NO_2)_2OH(H_2O)_2$ and $RuNONO_2(NO_3)_2(H_2O)_2$ were reported as very stable and commonly found in nuclear waste solutions by several authors. Yet no firm thermodynamic data for these two complexes were located in the literature. When the data are determined, they may drastically change the order and speciation for ruthenium solution species reported in Section 3.

6. The generation of Kd data that can be used in a comparative mode.

As mentioned earlier, an attempt was made to evaluate and select the best Kd values from the literature in writing Section 3. However, the experimental conditions, including soil, rock and solution characterization, were only sketchily given, or not given at all in most cases. Hence, the Kd values in Section 3 are the best available, but evaluation of these data by any objective methodology would result in discarding a large number of them. The requirements for determination of a Kd value that could be used in a comparative mode were listed in Section 2. A program to determine such Kd values is now underway by the Office of Waste Isolation of the Department of Energy.

7. Maintenance of a bank of such Kd data.

A bank of the Kd data should be maintained and kept current. The data could be computer-stored and made available to all personnel concerned with waste management upon request. The present system has resulted in using unevaluated Kd values that are often not applicable to the case in point.

If Kd values for biotite, quartz and orthoclase are known, a computed resultant Kd value for a granite, for example, should be possible if comparable surface areas are equated and if the biotite, quartz and orthoclase content of the granite are known. If the granite is composed of 25% quartz, 65% orthoclase and 10% biotite, and surface areas of minerals and rocks are similar, then (0.25) (quartz Kd) + (0.65) (orthoclase Kd) + (0.10) (biotite Kd) should equal the granite Kd value. There is no evidence in the literature that the above hypothesis has ever been tested. Until Kd determinations are placed on a comparable experimental basis, there would be little point in attempting to test and apply it.

8. Determination of radionuclide adsorption and desorption reaction kinetics with soils and rocks.

Several authors that have equilibrated solutions containing radionuclides with soils or rocks for several weeks have reported that a considerable period of time was required to attain equilibrium. Kinetic studies 1) could indicate radionuclide adsorption mechanisms, 2) could help in separating adsorption rates due to different mechanisms, and 3) would help in increasing the confidence in extrapolating the predicted results into the future.